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TITANIUM

ITS OCCURRENCE, CHEMISTRY, AND TECHNOLOGY

By

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DEDICATED
AS A MEMORIAL TO MY FATHER
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PREFACE

The purpose of this book is to meet the need for a comprehensive working reference volume on titanium, whose ever-increasing possibilities are attracting widespread interest. An endeavor has been made to produce such a book, one which will adequately and completely meet the requirements of all interested in the sources, chemistry, and technology of this element, and in its growing range of applications.

Titanium is already important commercially, not only as a white pigment material, but also in metallurgy, in ceramics, in the electrical industry, and as the metal itself. Metallic titanium is light, strong, tough, and noncorrosive. It has the desirable properties of both stainless steel and the strong aluminum alloys, which recommend it for many industrial applications. Very desirable gem stones have been produced from titanium dioxide. The element has many other uses beyond those briefly indicated here.

For a number of years the author has been engaged in research on titanium. In the course of his work he nowhere found an orderly, systematic collection of information having to do with the various phases of the subject. To meet this practical need, abstracts of published articles and of patent information were searched out and collected, and if not available in journals they were individually prepared. All these items have been arranged according to subject matter. They are here presented in such form as to make them readily available for consultation by those having an interest in any aspect of the subject.

Every effort has been made to achieve completeness of presentation. Abstracts of the entire literature of titanium, in all languages, have been carefully scrutinized, and the essential information has been incorporated into the text. All phases of the subject have been exhaustively covered in this manner, except the analytical chemistry of titanium, which is treated in a more general way, since an earlier work deals primarily with this phase. Precise references to all the material consulted will be found under the caption *Literature Cited*. These notations cover the field completely, up to the time of going to press.

CONTENTS

ILLUSTRATIONS

TABLES

TITANIUM

Chapter 1

THE DISCOVERY OF TITANIUM

The element titanium was discovered by the Reverend William Gregor[1] in 1790. Gregor was born in the county of Cornwall, England, in 1762. He studied at Oxford, earning the A.B. degree in 1783 and the A.M. degree in 1786, both from St. John's College. His classical and mathematical attainments, which were of the highest order, procured for him the most distinguished honors at the university. In 1789 he was collated to the rectory of Deptford, and in 1793 he was presented to the vicarage of Bratton Clovelly in Devon. Soon afterwards he transferred to the rectory of Creed, where he finally fixed his residence. In addition to his ecclesiastical duties he found time to continue his mineralogical and geological interests, and he was one of the founders and an active member of the Geological Society of Cornwall. The later years of his life were embittered by bodily suffering. He died of tuberculosis at Creed in 1817.

Berzelius,[2] in his letters, mentioned Gregor several times in connection with the discovery, analysis, and properties of minerals, and referred to him as a "celebrated mineralogist."

In 1791 Gregor communicated to the *Journal de Physique* the description and chemical analysis of a black magnetic sand found in the parish of Menaccan, six miles south of Falmouth, in Cornwall. The analysis showed almost 50 per cent of a white metallic oxide, up to that time unknown to chemists.[3] The sand was given the name *menaccanite* from the locality, and the new metallic oxide recovered from it was christened *menaccine* by R. Kirwan.[4]

Little interest was shown in the discovery for several years until Klaproth,[5] in 1795, noticed the close agreement between Gregor's account of menaccine and the findings of his own investigations of the oxide extracted from "red schorl" (rutile) from Hungary. The identity of the two substances was soon established, and Klaproth, acknowledging Gregor's priority, applied the temporary name *titanium* to the new element with the following comment: "Wherefore no name can be found for a new fossil (element) which indicates its peculiar and characteristic properties, in which position I find

myself at present, I think it is best to choose such a denomination as means nothing of itself and thus can give no rise to any erroneous ideas. In consequence of this, as I did in the case of uranium, I shall borrow the name for this metallic substance from mythology, and in particular from the Titans, the first sons of the earth. I therefore call this metallic genus, titanium." This "temporary" name has been retained, however, and it now appears to have been an appropriate selection.

In those pioneer investigations the finely ground ore was leached with hydrochloric acid to remove the iron, the dried residue was fused with sodium carbonate, and the melt was taken up in dilute hydrochloric acid. On treatment with zinc or tin the solution assumed a bluish or reddish color, but on exposure to air it again became colorless. An attempt to concentrate the solution by heating it on a sand bath resulted in a turbid suspension, resembling milk in appearance, which could not be cleared up by the addition of more acid. This property was the basis of the first analytical procedure developed; the solution was boiled to effect hydrolysis and the precipitate of hydrous titanic oxide was washed, dried, and weighed. Samples of the white oxide calcined alone became yellow, and in the presence of charcoal it became blue. It produced a yellow enamel color and was insoluble in acids, but it was soluble after fusion with an alkali. The new element showed a strong tendency to combine with oxygen.

Gregor's analysis of the black sand—oxide of iron 51.00 per cent, oxide of titanium 45.25 per cent, silex 3.50 per cent, and oxide of manganese 0.25 per cent—corresponded to that of the mineral ilmenite.

It is interesting at this point to note that the fundamental chemical reactions on which the present-day titanium pigment industry is based were known by both these pioneer investigators before 1800, although it was not until 1918 that these pigments were available commercially on the American market.

Chapter 2

THE OCCURRENCE OF TITANIUM

Titanium is ninth in abundance [1] of the elements making up the lithosphere, the ten-mile-thick crust of the earth, and accounts for 0.62 per cent of the total. It is exceeded in amount only by oxygen, silicon, aluminum, iron, magnesium, calcium, sodium, and potassium, and with the exception of these it comprises a larger proportion of the known terrestrial matter than all other metals combined, including zinc, copper, and lead, which are generally thought of as being quite common. Titanium is five to ten times as abundant as the well-known nonmetals, sulfur and phosphorus.

Rocks and Minerals

Titanium is a persistent constituent of practically all crystalline rocks and of sediments derived from them. Of 800 igneous rocks analyzed in the laboratories of the United States Geological Survey, 784 contained this element. It is present in most minerals, and it makes up the principal metallic constituent in an important group, the most common of which are ilmenite, rutile, arizonite, perovskite, and sphene or titanite.

Krugel and Retter [2] found 0.02 to 0.10 per cent titanium dioxide in phosphate rock from Florida, Curaçao Island, and North Africa. Apatite concentrate from the Chibinsk deposits of the Union of Soviet Socialist Republics contained 0.2 to 0.5 per cent. Forty-six samples of phosphate rock, representing practically all types available in the United States, showed 0.03 to 0.36 per cent. [3] The proportion was higher than that found in characteristic samples of bone ash. The element was detected in a radioactive bituminous mineral from the Boliden mine. [4] Spectrographic studies showed the presence of titanium in diamonds [5] and in gold. [6]

Soils

Dunnington [7] analyzed soils from many parts of the world and pointed out the wide distribution of titanium dioxide. From this work he estimated the average content of soils of Virginia as 1.57

per cent, of those of the remainder of the United States as 0.85 per cent; of Asia as 0.90 per cent; and of Europe as 0.54 per cent. Although data on the titanium dioxide content of soils from various parts of the world show wide variations, in a great majority of localities the values fall between the limits of 0.50 and 1.50 per cent. Frequently a considerable variation is also found in the strata or horizons of a given profile.[8]   Geilmann[9] detected this constituent in all soil samples he examined.   The proportion was highest, up to 1.0 per cent, in clay soils, progressively less in loam and sand, and lowest in soils of the calcareous type. The titanium content of the principal soil zones of the European part of the Union of Soviet Socialist Republics was reported to vary from 0.24 to 0.79 per cent.[10] Arable or desert soil contained the lowest proportion.   New Zealand soils[11] ranged from 0.25 to 1.5 per cent; the heavy loam and clay varieties contained the highest proportion.   This constituent has also been reported in the soils of the Maritime Alps along the Mediterranean,[12] in those of the cane-growing regions of India around Delhi,[13] and in the soils of Brazil.[14]   The lateritic soils of Savaii Upolu, Western Samoa, contain an unusually high proportion,[15] from 7.8 to 12.0 per cent, and 2.33 per cent was reported in the soils of the historic island of St. Helena.[16]   This oxide was found in deep well borings at a depth of 4490 feet, and in the deep-sea dredgings of the *Challenger*.[17]

Clays

According to Charrin,[18] all clays contain titanium dioxide. Kaolin was found to average 0.28 per cent, and white clays 0.88 per cent.[19]   Deposits in Wyoming[20] showed an average of 0.23 per cent, and typical flint clays from Orange County, California,[21] had 1.0 to 1.2 per cent. Alabama clays[22] were found to contain titanium in the form of ilmenite, and this constituent could be removed by tabling.   Twenty-seven samples from Finland[23] averaged 0.68 per cent titanium dioxide.   A series of primary clays from the Union of Soviet Socialist Republics[24] contained from 0.22 to 1.35 per cent, and a similar series of secondary clays showed 0.94 to 2.72 per cent, probably as rutile. Kaolin from the Usol, Irkutsk District,[25] contained from 0.3 to 1.03 per cent.   Similar proportions have been reported in the clays from San Paolo, near Rome,[26] and in the fire clays of Wales.[27]   Much higher amounts, up to 15 per cent titanium dioxide, occur in the ceramic clays of Hawaii,[28] and from 11 to 27 per cent in the clays of the Sudetenland.[29]   Isomatsu[30] reported

0.06 per cent of this oxide in bentonite from Japan. Titanium occurs as a minor constituent of most bauxites. For example, deposits in Bohemia [31] showed 4.6 per cent of the dioxide, those in Brazil [32] 2 per cent, and those in the north Urals,[33] 2 per cent.

It occurs as sphene in English fuller's earth.[34] Small proportions have been reported in the glauconites of Missouri.[35] Aplite,[36] a ceramic raw material from Virginia, contains 23.8 per cent. Hart [37] found up to 0.34 per cent of the dioxide in Portland cement, and 1.34 per cent in alumina cement.

Coal and Oil

Titanium is a common constituent of coals.[38] The ash of representative samples of anthracite coal from Pennsylvania [39] contained 1.0 to 1.8 per cent of the dioxide, and that of British coal [40] showed up to 3.0 per cent. This constituent has also been identified in the ash of German brown coal [41] and of peat from North Carolina,[42] and it has also been detected in the coals of the Charleroi basin in Belgium.[43] The ash of five samples of crude oils used in Germany [44] averaged 0.1 per cent of this constituent.

Water

The titanium content of natural waters is of the order of 10^{-7} to 10^{-6} per cent.[45] It has been detected by spectrographic methods in sea water,[46] in waters of the Río de la Plata in Argentina,[47] and in those of the Danube.[48] Very small amounts have been reported in the waters of the hot springs of Japan,[49] in many Spanish medicinal waters, and in the city water supply of Buenos Aires.[50]

Volcanoes and Meteorites

Noteworthy amounts of titanium dioxide were found in the volcanic dusts of Mount Pelée,[51] in the fumarole sublimation product from the crater of Vesuvius, and at Kilauea.[52] It has been detected in many meteoric stones.[53] The Perpeti meteoric shower [54] of May 14, 1935, showed 0.16 per cent; the Saratov meteorite,[55] which fell on September 6, 1918, contained 0.12 per cent in the magnetic fraction. A meteorite which fell on December 29, 1937, at Rangala, India,[56] contained 0.08 per cent, and another which fell in Ekely, Sweden,[57] on April 5, 1939, contained 0.22 per cent.

Sun and Stars

According to Lockyer,[58] the presence of titanium in the atmosphere of the sun was discovered by Thalen with the aid of the spectroscope as early as 1886. Later work confirmed the earlier finding and indicated that the element existed in the ionized form.[59] From the intensities of the lines of a number of elements, including titanium, the temperature of the solar atmosphere has been determined to be between 3500° and 5000° C.[60]

Lines corresponding to titanium have been observed in the spectra of many stars.[61]

Plants

The widespread distribution of titanium is by no means limited to rocks and minerals. Fifty samples of legumes, grains, vegetables, trees, and shrubs examined in the laboratories of the U. S. Department of Agriculture contained amounts up to 0.017 per cent.[62] Geilmann[63] examined twenty-three plants and plant parts, and of these cacao beans only showed no titanium. Potato tubers gave only a trace, and the ashes of the others contained up to 0.27 per cent of the dioxide. Green plant parts showed the highest proportions. Headden[64] reported 0.08 per cent titanium oxide in the ash of potato tubers and suggested that that in the ash of field-grown plants may have been derived from dust and soil blown upon them. The titanium content of tobacco is relatively high, while that of alfalfa is low.[65] Spectrographic examination revealed a higher percentage in the ashes of nodules than in the ashes of the roots of leguminous plants.[66] Titanium has been detected in samples of wire grass,[67] in both cryptogamic and phanerogamic plants,[68] and in the filter-press cake from a sugar factory on Manui Island, Hawaii.[69] According to Bertrand and Voronca-Spirt,[70] most of the titanium in seeds is concentrated in the tegument. Buckwheat and leguminous plants were found to be relatively rich in this constituent and contained considerably higher proportions than ordinary cereals; peanuts and hazel nuts were much poorer, but more was detected in walnuts and coconuts. Foodstuffs, such as the edible part of fruits, the roots of carrots, and the tubers of potatoes were poor, while onions and similar bulbs contained distinctly higher proportions. In these products the titanium content varied from one part in 10,000,000 to one part in 200,000 parts of the fresh weight. The element has also been reported in cotton seed,[71] in red clover,[72] and in the ashes of sunflower seed, horse chestnut, walnut, pumpkin,

peanut, wheat flour, and hen's eggs.[73] Appreciable amounts were found in the ashes of various kinds of wood.[74]

Animals

Baskerville [75] found that human flesh contains 0.0325 per cent of titanium dioxide, human bone a trace, beef flesh 0.013 per cent, and beef bone 0.0195 per cent. Amounts between 0.0015 and 0.011 mg. per 100 g. were reported in all organs of the human body,[76] the largest proportions being found in the lungs,[77] probably an accumulation from particles of titanium dioxide suspended in the air. It has also been detected in the bodies of the horse, calf, sheep, hog, and rabbit.[78] All animal tissues examined by Chuiko and Voinar [79] contained proportions ranging from 0.001 to 2.0 mg. per 100 g. The lungs, hair, liver, and kidneys showed the higher proportions.

Titanium has been found in a variety of sea creatures.[80] A number of specimens of fish [81] that were examined contained 0.3 to 0.9 mg. per kg., and various varieties of shellfish contained even higher proportions.

The titanium content of land and marine plants and animals and of fresh-water organisms varied from 0.00001 to 0.01 per cent.[82] Plants contained a slightly higher proportion than animals. Small amounts have been detected in the teeth [83] of man and the lower animals. Berg [84] detected small proportions in many foods and in excreta.[85] Spectrographic analyses of the ash of human and cow's milk [86] from various countries have consistently shown the presence of titanium. Samples of cow's milk in the Union of Soviet Socialist Republics [87] contained 0.001 per cent.

Chapter 3

GEOLOGY AND MINERALOGY OF TITANIUM

Titanium is a characteristic constituent of igneous and metamorphic rocks and of sediments derived from them. The chief mineralogical occurrences are as oxides, titanates, and silicotitanates, although the element is present in many silicates and less commonly in niobates and tantalates. In general, rock magmas rich in silica and poor in the base-forming elements, iron and magnesium, deposit their titanium component as oxide. Those containing relatively high proportions of calcium and silicon yield calcium titanate; those highest in iron and lowest in acid-forming oxides (silica) yield the iron titanates, ilmenite and arizonite. In silicates, titanium either replaces silicon in the acid radical or enters as a weak base-forming element. Titanium is often associated with magnetite and hematite, and it may make up a considerable proportion of such deposits.[1] Sundius[2] attributed the concentration of titanium in residual magmas to the presence of titanium tetrachloride and tetrafluoride, which hydrolyze to yield the dioxide, and to the occurrence of alkali silicates rich in titanium, which cause the formation of the alkali titanium silicates in the nepheline syenites. Lundegardh[3] studied the effect on the concentration of titanium of the time at which a mineral is formed during the crystallization differentiation.

Oxides

As the stable dioxide, titanium occurs in nature in three crystal modifications corresponding to the minerals rutile, brookite, and anatase or octahedrite, although the latter two are relatively rare.[4] Rutile[5] crystallizes in the tetragonal system, commonly in prismatic crystals and often in slender acicular ones. It has a distinct cleavage, subconchoidal to uneven fracture, metallic-adamantine luster, hardness of 6.0 to 6.5, and specific gravity of 4.18 to 4.25. The color is usually reddish to brown, sometimes yellowish, bluish, or black, and rarely green. It is transparent to opaque and gives a pale brown streak. Iron and vanadium are usually present in proportions up to 10 per cent.

Brookite is of the orthorhombic crystal form. It has a specific gravity of 4.0, hardness of 5.5 to 6.0, and molecular volume of 20.0. The color is yellowish, reddish, brown, or iron black.

Anatase or octahedrite crystallizes in the tetragonal system. It has a specific gravity of 3.82 to 3.95, hardness of 5.5 to 6.0, and molecular volume of 20.5. The color varies from brown to indigo-blue to black. All three modifications in the pure state correspond to the chemical formula TiO_2.

Rutile is found in all types of rocks, igneous, metamorphic, and sedimentary. It is a constituent of eruptive rocks, pegmatite dikes, contact metamorphic deposits, regionally metamorphosed rocks, and veins both metalliferous and nonmetalliferous.[6] Although rutile occurs as a pyrogenetic mineral in eruptive rocks, it is more common in the metamorphics and is found in gneiss, mica schist, amphiboles, and phyllites,[7] and less commonly in granular limestones and dolomites.[8] In the crystallines it appears both as a pyrogenetic constituent and as an alteration product. In clastic deposits [9] (sediments) the most important occurrences are in beach and stream sands. In minute crystals and small quantity the mineral is found in some of the dark micas, as large crystals in quartz veins closely related to pegmatites, and in schists to which siliceous solutions have carried the titanium. The known large deposits are in pegmatites or in very closely related basic rocks such as kragerolite, a rutile-plagioclase rock. Apatite and albite are common associates.[10] Rarely rutile is found as a secondary mineral derived from ilmenite and titanite, and sometimes from certain of the ferro-magnesian silicates, especially biotite. It is relatively very stable, but it sometimes alters to leucoxene along with ilmenite.[11]

Brookite does not occur in fresh eruptive rocks, but is generally found in decomposed gneiss and quartz porphyry and in sedimentary deposits. It alters into rutile.

Octahedrite is never primary but is formed by the alteration of other titanium minerals. It has been observed under a great variety of conditions, as in granite, diabase, quartz porphyry, diorite, the crystalline schists, shale, sandstone, and limestone. Rutile is of pyrogenetic origin, while brookite and octahedrite occur only as secondary minerals.

All three modifications have been prepared synthetically. These experiments showed that rutile, the most stable form of titanium dioxide, was formed at the highest temperature; brookite at a temperature considerably lower; and anatase at a point still lower on the scale. These observations are in harmony with the known

occurrences of the three species as rock-forming minerals in nature.[12]

According to Walker,[13] the titanium in Transvaal lodestone is in the trivalent state. Because of this he suggested the name titaniferous magnetite, $(FeTi)_2O_3$. Rankama [14] reported that tantalum occurs in appreciable amounts in titanium minerals. Vanadium and chromium are also usually present.

Titanates

Of the many titanates, only a few are important industrially, particularly those of iron and calcium. Ilmenite [15] is a heavy mineral of metallic to submetallic luster, crystallizing in the rhombohedral class of the hexagonal system with specific gravity of 4.5 to 5.0, hardness of 5 to 6, and molecular volume of 30.4. The color is usually iron black, but it may be reddish to brown. The streak is black to reddish brown. It is opaque and slightly magnetic, cleavage is not developed, and fracture is conchoidal. The mineral is isomorphous with pyrophanite, magnesium titanate, which has the chemical formula $MgTiO_3$. It is rarely seen in good megascopic crystals in rocks but usually occurs as embedded grains and masses or plates of irregular outline. The chemical composition of natural ilmenite is variable, with the result that its constitution has been much discussed although it is generally regarded as ferrous titanate corresponding to the chemical formula $FeTiO_3$. Proportions of iron higher than the theoretical may be due to admixed hematite or magnetite, while an excess of titanium may be due to the presence of rutile. Studies of ilmenite samples from different sources indicate that the ferric oxide is not in chemical combination, but rather is held mechanically as inclusions or intergrowths. Watson and Taber suggested an isomorphous series $(FeTi)_2O_3$ in which the metallic components may vary widely, even grading into hematite. Singewald [16] has held that the titanium in titaniferous iron ores may be present as an integral part of the magnetite molecule itself, although most authorities believe that these ores are composed primarily of magnetite or hematite, with intergrowths of ilmenite. The latter view is strengthened by the fact that high-grade concentrates can be prepared by mechanical means from many titaniferous iron ores.

From a study of X-ray absorption edges, Hamos and Shcherbian [17] obtained values for the titanium present corresponding to the quadrivalent state, and concluded that the chemical formula $FeTiO_3$

represents divalent iron and tetravalent titanium, although from a chemical standpoint these values might be three and three respectively. This is also substantiated by chemical analysis.

Ilmenite is widely distributed in nature. It is formed in igneous rocks, in pegmatites, in contact metamorphic deposits, under regional metamorphic conditions, and in deep veins.[18] The most important occurrences are in coarse-grained gabbros and anorthosite where the ilmenite is frequently segregated into large masses. The metamorphic rocks [19] which most commonly contain it are gneiss, mica schist, and amphibolite. The mineral appears in most igneous rocks and their lava forms, although its chief occurrences are in those varieties that are poor in silica. In addition to being an essential constituent of diabase, basalt, diorite, and gabbro, it is found in the acid crystalline rocks such as granite and syenite, in andesite and more basic lavas. Along with magnetite it is one of the first minerals to separate from magmas.[20] The large masses of ilmenite found in many parts of the world associated with more or less magnetite, olivine, pyroxene, and soda-lime feldspar are simply phases of the rock itself formed by concentration from the original magma. Near such ore bodies, consisting of a mixture of ilmenite and ferromagnesian silicates, the dark-colored basic components first increase and the feldspar finally disappears.[21] The mineral as flat, imperfect crystals occurs in small quantities in quartz veins, although its most common form in large deposits is as plates intergrown along the cleavage planes of magnetite. These plates are often microscopic in size. Ilmenite-magnetite and ilmenite-hematite in large bodies are found only with gabbros, anorthosite, and similar rocks.[22]

Pseudobrookite,[23] ferric orthotitanate, corresponding to the chemical formula $Fe_8(TiO_4)_3$, crystallizes in the orthorhombic system, has a specific gravity of 4.39, hardness of 6, and molecular volume of 127.5. The color varies from dark brown to black. It occurs as a rare accessory mineral in certain eruptive rocks of the andesite, trachyte, basalt, and nephelinite type.

Arizonite,[24] a ferric titanate having the chemical formula Fe_2TiO_6 is probably monoclinic. It has a dark steel-gray color, metallic luster, and brown streak. Thin sections, which are transparent, appear deep red in transmitted light. Although the mineral seems to form a larger part of some sands classified as ilmenite, particularly those of Quilon, India, and Senegal, West Africa, it has only comparatively recently been recognized as a distinct mineral. Chromic oxide, usually present, may replace ferric oxide in the molecule.

Perovskite,[25] calcium titanate, of the chemical formula $CaTiO_3$, crystallizes in the isometric system. The molecular volume is 34, specific gravity 4.0, hardness 5.5. The color is yellow, ranging through orange and brown to grayish black. It is found in both eruptive and metamorphic rocks. In the former it is associated with melilite, leucite, nepheline, and some peridotites, and is among the earliest secretions. Other occurrences are in chlorite schist, limestone, and quartz gneiss. It may be derived from titanite and may alter into titanic oxide.

Geikieilite, magnesium titanate, of the chemical formula $MgTiO_3$, and pyrophanite, manganese titanate, having the chemical formula $MnTiO_3$, are rare as separate minerals but of interest because they form intergrowths with ilmenite.

Silicates

Titanite or sphene [26] is titanium calcium silicate that corresponds to the chemical formula $CaTiSiO_5$. It crystallizes in the monoclinic system, has a specific gravity of 3.54, hardness of 5.0 to 5.5, and molecular volume of 55.5. The color varies from yellow to green, red, brown, gray, or black. Pyrogenetic titanite is found along with the oldest secretions in the more siliceous rocks such as granite, diorite, syenite, and trachyte, and is abundant in phenolites and elaeolite syenites. It is also formed as an alteration product of rutile or ilmenite and is frequently associated with chlorite. Alteration of titanite into rutile has been reported.

The name silicoilmenite [27] has been suggested for a red-brown mineral forming polysynthetic intergrowths with ilmenite. It is found in the Ilmen Mountains, Union of Soviet Socialist Republics, and is reported to be a solid solution of a silicate or silica in ilmenite.

Chapter 4

MINERAL DEPOSITS THAT YIELD TITANIUM

Massive Ilmenite

In contrast to its widespread occurrence, only a few minerals bearing titanium, particularly ilmenite, rutile, arizonite, titanite, and perovskite, are known to occur in bodies large enough to be of economic importance.

VIRGINIA. Pure ilmenite in place in rich minable ore bodies is found in western Virginia [1] in an unusual rock mass known as nelsonite. In it ilmenite and apatite, or rutile and apatite, are the essential minerals. Phlogopite, quartz, pyrite, pyroxene, and hornblende are, however, frequently present as accessories. These nelsonite bodies, which have the form of dikes, are enclosed in a biotite schist of the Lovington granite gneiss. Apatite appears to have been the primary mineral and to have been replaced by ilmenite or rutile until in some places only small rounded pellets of the original mineral are left.

Another type of deposit is known in the same area in which the titanium minerals occur as disseminations in the anorthosite. The origin of the ore bodies is not altogether clear. Ross [2] concluded that both types were not of pyrogenetic origin, but that they were deposited by hydrothermal invading solutions believed to have been derived from a deep-seated, highly ferromagnesian rock, probably itself a differentiate from the same magma as the anorthosite. Ferrous iron was first abstracted from the carrying solutions to form ferromagnesian silicates and ilmenite. Magnesium and titanium traveled farther and deposited rutile and magnesium silicate. At greater distances the feldspar was completely altered without any marked change in its chemical composition. Davidson, Grout, and Schwartz [3] concluded that the ilmenite deposit was an irregular fingering dike intruded into anorthosite and later sheared and hydrothermally altered.

In adjacent Amherst and Nelson counties, in Virginia,[4] are nelsonite bodies large enough to be of economic value as producers of ilmenite. By far the largest of these yet discovered is located in Am-

herst County, across Piney River from the railroad station of the same name. This dike-like mass outcrops 70 to 80 feet high for a distance of 350 feet along the river in a bluff at the edge of an old terrace. The maximum surface width of 400 feet extends for 1300 feet to the southwest, then tapers within the next 600 feet to a width of less than 100 feet. A tail, 60 to 100 feet wide, extends for more than 1000 feet farther. Since the dike dips with the schists about 45 degrees to the southeast, the surface outcrop of 400 feet represents an actual thickness of the main body of about 283 feet. The tail is 28 to 71 feet thick. The ore, which has been proved to a depth of 400 feet, appears to continue deeper. Weathering has extended about 75 feet below the surface to such an extent that the nelsonite appears as a rather rusty rock, soft enough to be crushed in the hands. Deeper, however, it becomes harder. The ilmenite is a clear black, the apatite is comparatively clear, and there is enough chlorite to give the rock a greenish cast. Pyrite in small amounts is found along the cracks.

The original rock contains 18.5 per cent titanium dioxide, and after separating the apatite, which accounts for all the gangue material, it yields a concentrate containing 43.7 per cent titanic oxide.[5] The unweathered rock is said to be quite amenable to treatment, although the weathered material is more easily worked. This deposit, to a depth of 400 feet, contains 24,000,000 tons of nelsonite carrying more than 4,400,000 tons of titanium dioxide. For a number of years large quantities of apatite, obtained as a by-product in the ilmenite mining, have been employed as the raw material for the manufacture of primary calcium phosphate for use in the manufacture of baking powders.

About a mile and three quarters down Tye River, below Massie's Mill, there is a hard vertical dike of nelsonite 60 feet wide and 600 feet long. Another dike of about the same width, but shorter, occurs on Hat Creek. Two miles farther up the same creek is a dike that is reported to be 40 feet thick and of unknown but considerable length. These deposits are reported to contain 30 per cent titanium dioxide, and the available reserve has been estimated at 2,000,000 tons of such ore. In addition, many smaller dike-like bodies of nelsonite have been reported in both counties, as well as in Roanoke County.

NORTH CAROLINA. A deposit of nearly pure ilmenite, slightly intermixed with talc and serpentine, occurs about one mile north of Finley, Caldwell County, North Carolina.[6] The ore body is lenticular in shape, 45 feet wide at the best exposure, and outcrops along

the strike for half a mile. It is apparently a part of a peridotite intrusion along a fault plane dipping 35 degrees to the southeast. The country rock is sericite schist consisting of small particles of ore in a matrix made up chiefly of fibrous and scaly aggregates of chlorite, serpentine, and talc. A sample of the ore from this deposit analyzed 49 per cent titanium dioxide. Three fourths of a mile to the southeast a similar ore body outcrops for nearly three fourths of a mile. It is 25 feet thick but is not so rich as the first deposit.

Ilmenite-Magnetite

UNITED STATES. In the United States the largest deposits of titaniferous iron ores are in the Adirondack Mountains of New York State.[7] The occurrences are large bodies of ilmenite-magnetite carrying from 7 to 23 per cent titanium dioxide and enclosed in the country rock of anorthosites and dark gray gabbro or norite. The Sanford Hill deposit in Essex County [8] carries 62.8 per cent magnetite and 30 per cent ilmenite. By magnetic separation, one ton of this ore gave two thirds of a ton of an iron concentrate containing 7 per cent titanium dioxide, and the tailings yielded one fifth of a ton of ilmenite containing 49 per cent titanium dioxide and 34 per cent iron. The proved ore reserve of this deposit alone has been placed at 100,000,000 tons.

After standing idle for many years, this deposit was reopened in 1941 to supply the domestic demand for ilmenite formerly obtained from India but cut off by war conditions.[9] The ore, as mined, consists of a mixture of ilmenite, magnetite, feldspar, hornblende, pyroxene, garnet, and biotite, with a small amount of the vanadium mineral, coulsonite.[10] Grinding to 20 mesh is required for effective separation of the mineral components. A magnetic concentrate, rich in iron and vanadium, was obtained from low intensity, wet magnetic separation, and an ilmenite concentrate was obtained from the nonmagnetic tailings by hydraulic classifiers and tables. This ilmenite product, containing 38 per cent titanium dioxide, was improved in grade to 45 per cent on high intensity, dry-magnetic separators. The original ore contained 16 per cent titanium dioxide,[11] and in addition to the ilmenite concentrate, it yielded magnetite containing 56 per cent iron with 0.12 to 0.17 per cent sulfur and only a trace of phosphorus.

Another extensive deposit of titaniferous iron ore is located in Lake and Cook counties, Minnesota.[12] The titanium content ranges from 3 to 20 per cent, although samples with a yield as high as 40
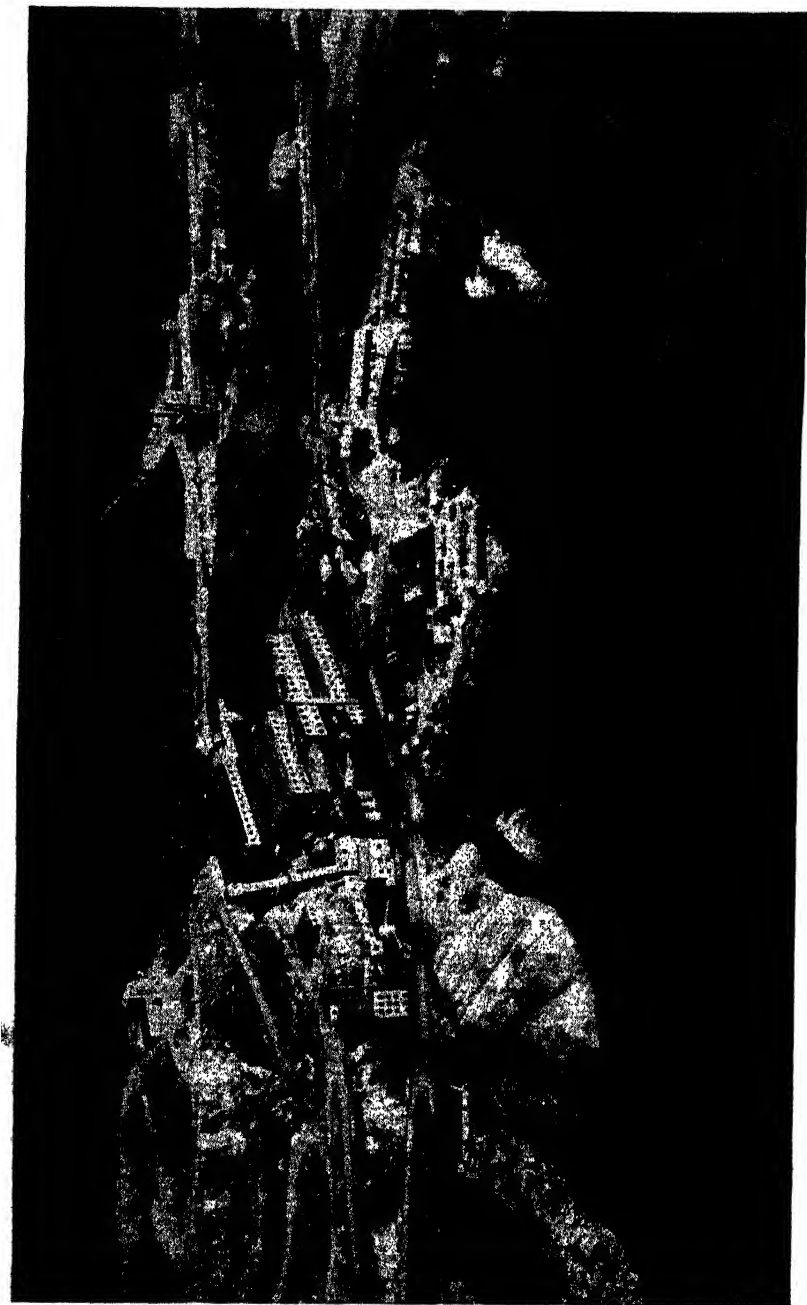
Figure 1. Ilmenite mine and mill at Tahawus, Adirondack Mountains, New York
(Courtesy National Lead Company)

per cent have been obtained. Most of the ore-bearing rock contains very dark ferruginous minerals as gangue material, which closely resembles the ore. Few of the outcrops exceed 10 feet by 100 feet in area, although the number of small exposures is quite large.

Another large deposit of such ore in the United States is in Cumberland, Rhode Island, where there is an outcrop 600 feet wide and 1500 feet long. A concentrate containing 22 per cent titanic oxide and 54 per cent iron can be produced by magnetic separation.

On Chugwater Creek, 8 miles west of Iron Mountain Station, Wyoming, on the Colorado and Southern Railroad, there is an extensive igneous dike of solid titaniferous magnetite one and one fourth miles long with an average width of 175 feet (100 to 200 feet), in anorthosite with some associated granite. Most of the analyses show 22 to 23 per cent titanium dioxide, although some much lower values have been reported.[13] Satisfactory concentration of the ore requires several steps. There are, in addition, several dike-like bodies in the vicinity.

Composite drill cores from the Choteau titaniferous magnetite deposit in Teton County, Montana, analyzed 43.7 per cent iron, 7.2 per cent titanium dioxide, 0.05 per cent sulfur, 0.018 per cent phosphorus, 0.5 per cent manganese, 17.0 per cent silica, 1.6 per cent calcium oxide, 1.2 per cent magnesium oxide, and 5.2 per cent alumina.[14] Magnetic concentration of the 100-mesh material increased the percentage of iron to 60.6, but lowered the titanium dioxide content only to 6.6 per cent.

Large deposits of titaniferous magnetite are known in the San Gabriel Mountains, Los Angeles County, California. The principal occurrences are on the ridge south of Soledad Canyon, extending 5 miles from Lang to Russ Siding, and also in the area southwest of Mount Gleason and north of Tujunga Canyon. The ores of this region are associated with rocks of the gabbro family, and the largest bodies are contained in rocks composed chiefly of labradorite in coarsely crystalline, granitoid aggregates that have been called anorthosite by the Canadian geologists. (Anorthosite is a nearly pure plagioclase rock in which labradorite is the prominent feldspar.) These ores consist almost entirely of magnetite and ilmenite, with little visible gangue, and the titanium dioxide content is said to range from 11 to 25 per cent.

Titaniferous iron ores are found in Colorado at Caribou Hill, Boulder County, at Iron Mountain in Fremont County, and on Cebolla Creek, south of Powderhorn, in Gunnison County. Analyses of samples from these deposits show 8.5, 12.95, and 9 to 36 per

cent titanium dioxide, respectively. The ore is not well adapted for magnetic concentration. Numerous smaller deposits of titaniferous magnetites, associated with anorthosite and believed to be magmatic segregations, occur in the Wichita Mountains of Oklahoma.[15] An average of five samples gave 7.31 per cent titanium dioxide, although values up to 16 per cent have been obtained. Large quantities of titanium ore, of satisfactory commercial grade, were discovered comparatively recently in Hidalgo County, New Mexico,[16] near the Arizona border. The ore body is a replacement deposit of contact metamorphic origin, and the areal extent averages 70 feet wide by 1000 feet long. Other occurrences of iron ores rich in titanium have been reported in North Carolina, South Carolina, Tennessee, and New Jersey.

NORWAY. Extremely large deposits of massive ilmenite-magnetite ore are found in the southwest part of Norway between Egersund and Sogndal, and are known as Kohldahl, Kyland, Storgangen, Blaafjeld, and Lakesdal.[17] One of the largest and purest of those so far described is the Blaafjeld deposit, Jossing Fjord, in Sogndal, south of Egersund. This ore contains from 40 to 45 per cent titanium dioxide and averages 42 per cent. The available reserves, to a depth of 100 meters (327 feet), have been placed at 3,000,000 long tons. Some years ago ore from this region was shipped to England to be smelted for iron, and a short railroad was built to the coast. Since 1920, however, ilmenite has been the product sought and it was on this deposit that the titanium pigment industry was started.

The Lakesdal deposit near by is estimated to contain 225,000 long tons of ilmenite-magnetite carrying 35 per cent titanium dioxide. These bodies are long dikes of ilmenite-magnetite from 50 to 300 feet wide and of unknown thickness in gabbro formation. The best known deposit of titaniferous magnetite is located at Rodsand, on the southeastern shore of Tingvoldfjord, and has been worked for the iron values. Run-of-mine ore contains 6.0 to 7.5 per cent titanium dioxide, but this may be reduced to 1.1 to 1.35 per cent in the magnetic concentrate.

CANADA. Both ilmenite-magnetite and ilmenite-hematite are found in many places in Canada, although the best known occurrences are at St. Urbain, Charlevoix County, Quebec. According to Gillson,[18] these ore bodies are formed by replacement of the anorthosite with which the ilmenite is associated and were deposited by gaseous or liquid solutions which soaked through the rock. The
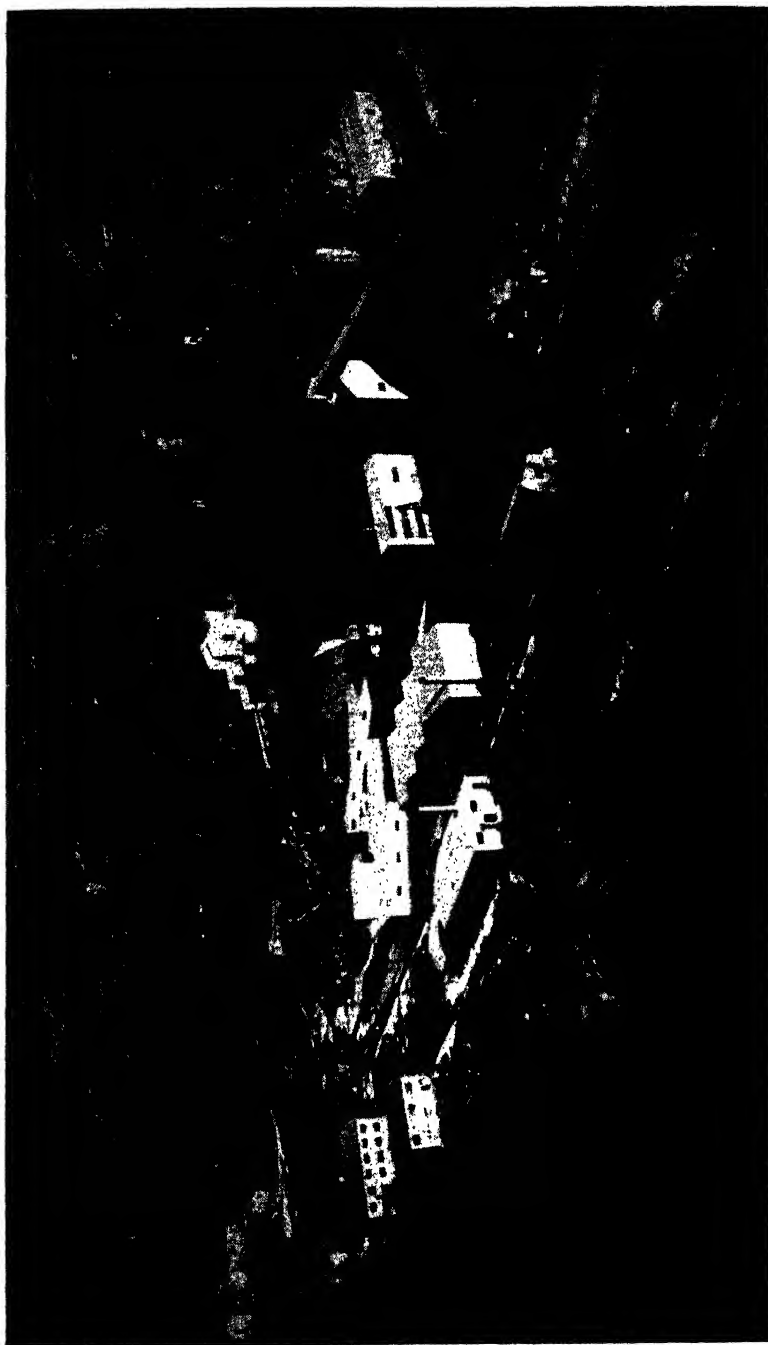
Figure 2. Ilmenite mine in Norway
(Courtesy National Lead Company)

original solutions were derived from the magmatic reservoir. Similar deposits, but without rutile, occur at Ivry, Terrebone County, also in Quebec. Ores from both localities contain 20 to 30 per cent titanium dioxide, although several thousand tons, presumably concentrates, carrying 35 to 40 per cent, have been shipped to Niagara Falls, New York, for the manufacture of ferrocarbontitanium.

Bodies of titaniferous magnetites, seldom containing more than 15 per cent titanic oxide, are known to occur near Lake St. John on the Saguenay River, on Bay of Seven Islands, along Seine Bay, and in the Rainy Lake region, Quebec. Other apparently less important deposits have been reported in Renfrew, Hastings, and Hamilton counties, and in the Nipissig district, Ontario.[19] An ore body more important as a source of iron and containing less than 4 per cent titanium occurs in the Rocky Mountains near Burmis, Alberta. All these deposits are magmatic segregations genetically connected with basic eruptive rocks of the gabbro family and generally irregular and uncertain in their mode of occurrence, a characteristic of titanic iron ore deposits the world over. Large bodies of titaniferous magnetite are known in the western part of Newfoundland. The ore contains 4 to 16 per cent titanium and as much as 65 per cent iron.

In 1948 large deposits of ilmenite and ilmenite-bearing iron ores were discovered in eastern Quebec, and plans for a $25,000,000 project to develop the ores was announced by Kennco Explorations, Ltd., a subsidiary of Kennecott Copper Corporation. These deposits, reported to carry millions of tons of ore, are near Lake Allard, 400 miles northeast of Quebec City. One report placed the proved reserves at 50,000,000 tons, others at still higher values.

UNION OF SOVIET SOCIALIST REPUBLICS. With the exception of the Scandinavian Peninsula, Europe is not rich in titanium deposits, although there are apparently extensive deposits of low-grade ores in the Union of Soviet Socialist Republics.[20] The main resources are the titaniferous magnetites in the Ilmen Mountains, a branch of the Urals, and it is from these mountains that the mineral *ilmenite* received its name. These ores, which contain 14 per cent titanium dioxide, 54 per cent iron, and 0.6 per cent vanadium pentoxide, are amenable to magnetic separation,[21] yielding a concentrate containing 42 per cent titanium dioxide and 37 per cent iron, and another product containing 64 per cent iron and 7 per cent titanium dioxide carrying 87 per cent of the original iron. Ore from the Kussinsk[22] area, containing iron 51.9, titanium dioxide 14.2, and vanadium pentoxide 0.66 per cent, ground to pass a 65-mesh screen and sub-

jected to wet-magnetic separation, gave an ilmenite concentrate representing 19.5 per cent of the original weight, which contained 45.3 per cent titanium dioxide, 35.8 per cent iron, and 0.34 per cent vanadium pentoxide. The Ural deposits are reported to carry 400,000,000 tons of available ore. Other important occurrences [23] have been reported near Khibine, on the Kola Peninsula, and near Gatskavo, in the Ukraine.

SWEDEN. The huge igneous sheets at Kirunavano, Sweden, contain a low percentage of titanium. Occurrences of titaniferous iron ore are known at Taberg. A deposit of ferro-orthotitanate at Sodra-Ulvon contains a large proportion of the mineral Fe_2TiO_4, not previously found in nature.[24]

FINLAND. The titanium ores of Finland have been described by Geiler.[25]

Occurrences have also been reported in Transylvania and in the Carpathian Mountains.

AFRICA. There are extensive deposits of magnetic iron ore, containing as much as 14 per cent titanium dioxide, in the Union of South Africa. Occurrences containing 10 per cent titanium dioxide and up to 40 per cent iron are found over a large area in the Transvaal, although the largest deposit is at Magnet Heights, north of Pretoria. Titaniferous magnetites, together with massive ilmenite, occur as veins and segregations in the norite of the Peninsula of Sierra Leone. Thicknesses of the former of more than 15 feet, and of the latter of 5 feet, have been observed. Occurrences have been reported in Rhodesia and in Dahomey. Ilmenite and rutile are associated with the diamond deposits of Sierra Leone.[26] Two deposits of titaniferous iron minerals of different types are known in Mozambique.[27] The larger consists of somewhat magnetic material, mainly titaniferous magnetite, and ilmenite with a titanium dioxide content of 10 to 13 per cent. Some goethite has been formed from the alteration of ilmenite. The smaller deposit contains ilmenite and magnetite in the form of grains 1 to 2 millimeters in diameter.

A deposit located near Betroka and consisting of an intimate mixture of ilmenite and hematite enclosed in gneiss contains 27 per cent titanic oxide; the quantity of the ore has been estimated at 3,500,000 tons. An occurrence of an ilmenite-magnetite mixture derived from gabbro is located in the valley of the Vongoabe River, a tributary of the Mahajlo. Extensive deposits of high-grade titaniferous magnetite occur at Liganga, in the undeveloped Njombe

district, Tanganyika Territory.[28] The reserve has been placed at 1,200,000,000 tons. Smaller deposits have been reported in the Belgian Congo.

Titaniferous iron ores of two varieties are found on the island of Madagascar.

ASIA. Deposits of titaniferous iron ores are known to occur in Manchuria, Korea, Indo-China, and India. Large quantities of titaniferous magnetite have been reported in the Mysore State of India. These ores, which contain 11.6 per cent titanium, have not been utilized. Ilmenite, together with titaniferous magnetite, occurs in segregated masses in pegmatite veins in the Mellore District, Madras,[29] in commercial quantities. Similar deposits have been reported in the Arabian Desert.[30]

Extensive beds of titaniferous magnetite occur north of Port Stevens in New South Wales, and ilmenite and rutile are found in some permian sediments of Western Australia, Australia.[31]

Beach Sands

As a result of the extreme stability of titanium minerals, particularly rutile, ilmenite, and arizonite, they are left behind as the country rocks are weathered and eroded away, and accumulate in the black sands of streams and beaches. These placer deposits are extremely important, since they are easiest and cheapest to work and have supplied a large part of the world production of titanium ores. Stream gravels are worked locally to a limited extent, but much the greater output is derived from ocean beaches. Natural concentration on some beaches has progressed to remarkably high degrees, for example, in the State of Travancore, India. In New South Wales, Australia, rutile, ilmenite, and zircon make up 75 per cent or more of the black sands. The mineralogical composition of the concentrate naturally depends upon the ratio of the heavy resistant minerals of the country rocks and upon the drainage area. For instance, it is impossible to get high-grade natural concentrations of ilmenite in localities in which the weathered rocks also yield large proportions of such minerals as garnet and magnetite, since these minerals accompany the ilmenite. Such a condition exists at Nome, Alaska, where large proportions of garnet are fed into the sea along with the ilmenite.

ASIA. At the present time the most productive beaches of the world are on the coast of the native state of Travancore, which makes up the western part of the southern tip of India. Two strips

along the shore line, one in the southern part of the state at Maravalakurichi and the other 80 miles to the north and 4 miles north of the well-known town of Quilon, are particularly rich.

The beach at Maravalakurichi, known to European residents as "M. K.," was first worked for monazite to supply the gas-mantle trade beginning in 1911, and ilmenite was largely a waste product. About 1924 the increasing demand for ores to supply the rapidly expanding titanium pigment industry reversed the situation, and up to 1934 nearly all the Indian production came from this beach. The heavy drain has largely depleted the rich reserves. Ore from this beach is usually designated broadly as "Travancore" rather than the more restricted and appropriate "M.K." The productive section, arcuate in form, extends for 6000 feet from a rocky headland at Muttum, westward toward the headland at Colachet, in the lee of which ocean-going steamers anchor while being loaded by natives from dugout canoes. Sand has been mined both from locally rich areas on the beach front, where it has been naturally concentrated by the waves, and from buried, highly concentrated seams, similarly formed at earlier stages in the development of the shore line. The ilmenite portion of the crude sands, as mined, ranges from 50 to 70 per cent, although the 6 or 8 feet of overburden that must be removed from the buried seams contains a much lower proportion. Mining methods are quite crude. The sand is loosened with a momite, a hoelike tool universally used in agricultural pursuits in India, placed in baskets, and carried by natives on their heads to cars, which deliver it to the concentration plants. A large part of the quartz is removed on wet tables. The sand is then dried in the sun and passed over dry tables and magnetic separators to remove zircon, monazite, rutile, garnet, and other minerals. This mixture is further treated to separate zircon and monazite, which are further concentrated to yield valuable by-products.

The second producing beach begins just south of Neendahara Inlet, 4 miles north of Quilon, and extends to Kayankulam Bar, 15 miles to the north. An interesting historical sidelight on the area is that at the time of Marco Polo's visit, about 1270, Neendahara Inlet was one of the busiest ports of the world. A large concentrating plant was erected at the village of Kovilthatam, 8 miles north of Quilon. Areas on the dunes, back from the shore north of Kovilthatam, produce on a moderate scale. Although usually referred to as ilmenite, the concentrates from this beach contain a large proportion of the mineral arizonite. The Maravalakurichi concentrate,

as shipped, contains 54 per cent titanium dioxide, while that from Quilon is higher, around 60 per cent.

In the Federated Malay States, a considerable proportion of ilmenite, along with zircon, accompanies the tin ore, cassiterite, in the placers and is obtained as a waste product from the mining operations. A large part of the ore comes from Perak, since the tin mining is concentrated there. At plants where magnetic separation is employed, almost pure ilmenite is produced incidental to the concentration of cassiterite. According to Hess,[32] the ilmenite is loaded on ships at a nominal cost and shipped to England for pigment manufacture. There are numerous deposits on the coast of Annam, Indo-China, and the magnetic sands of Ceylon are potential sources of ilmenite for commercial purposes.[33]

Workable deposits of ilmenite occur in Australia at Naracoopa, at the mouth of Fraser River on King Island, 60 miles north of Tasmania, in Bass Strait, and along the central eastern coast from Shoalhaven River, in New South Wales, toward Brisbane, in Queensland. The black sands of the Naracoopa beach, carrying ilmenite along with cassiterite, monazite, and gold, are 8 feet thick and yield a magnetic concentrate carrying 45 per cent titanium dioxide. Beach sands along the coast have been concentrated naturally by the action of waves, and these beaches have been worked intermittently for their tin, gold, and platinum content since the turn of the century. The largest deposits are north of Port Macquarie. Similar sands along the coast near Fitzroy, New Plymouth, New Zealand, contain 2.62 to 9.6 per cent titanium dioxide.[34] Water-sorted titaniferous iron sands on the beaches at Patea, South Taranaki, have been estimated at 12,250,000 tons.[35]

Remnants of old beaches extend a few feet above the present beach. According to Fisher,[36] reserves of ilmenite and rutile along the east coast of Australia are adequate for several years.

Japan has extremely large deposits of titaniferous magnetite sand derived from her many and widespread lavas and metamorphic rocks.[37] Such sands occur on most beaches of the main islands of Hondu, Kyushu, and Hokkaido. The richest deposits, which are on the east coast of Aomori and Iwate prefectures, Hondu, consist of thick layers of magnetic sand cemented with ferric oxide mud. The available reserves were placed by a government engineer at 10,000,000 tons, carrying, as mined, 20 to 30 per cent iron, 8 to 12 per cent titanic oxide, and 0.6 per cent vanadium pentoxide. These sands, which are amenable to concentration, give a product containing 60 to 65 per cent titanium dioxide. A strip 70 miles long and

20 miles wide, centering around Kuji, 100 miles from the north tip of the island of Hondu, has been raised above sea level and is blanketed with a layer of the titanium-bearing sands averaging 18 feet in thickness. Minimum available reserves of this region have been placed at 200,000,000 tons of ore. From X-ray studies, Ando and Nitto [38] found that the Japanese ilmenite-rutile ores have the rutile structure and consist of a solid solution of rutile and mossite. Several companies were producing ores in 1937 for the manufacture of titanium pigments and ferrochrometitanium.

Natural concentrations of magnetic-iron sands containing ilmenite are found along the coast of the Island of Java.

UNITED STATES. Sands at many places along the Atlantic, Pacific, and Gulf coasts contain titanium minerals, although the highest concentration is found along the east coast of Florida from the mouth of the St. Johns River to the town of St. Augustine. This occurrence consists of a complex black sand containing ilmenite, rutile, monazite, and zircon which have been concentrated naturally between low and high tides. A strip of the beach extending 3 miles north and 8 miles south of Mineral City, south of Jacksonville, was operated on a commercial scale for a number of years, beginning in 1918, but was abandoned in 1929 and is now the site of an attractive country club. There were reports that the deposit was worked out, but what appears to be a more likely explanation is that it was not able to meet the competition offered by the Travancore deposits. By a relatively simple washing and concentrating process, the mineralogical components of the sand were separated from one another. For a time ilmenite from this beach supplied the greater part of the requirements of the Titanium Pigment Company, Inc.[39] Around 30,000 tons of ilmenite and a few hundred tons of rutile were produced during this period. The principal beds occur on the back part of the beach at the foot of the dunes, and the heavy mineral content of the sands varies from 20 to 60 per cent.

Extensive deposits of heavy mineral sands in the Trail Ridge area of the north central part of the State of Florida contain ilmenite, along with rutile and zircon.[40] The ilmenite in this deposit, which has been classed as leucoxene, contains extremely fine-grained rutile. The mineral is sedimentary in origin, the original source having been the Piedmont area of Georgia and the Carolinas. The area, which is under a long-term lease by E. I. du Pont de Nemours and Company, is expected to supply the demands of the company for ilmenite.

Low-grade deposits of ilmenite-bearing sands occur in the southern part of Howard County, Arkansas.[41]

The beach sands of the entire Pacific Coast contain ilmenite in various proportions, together with magnetite, gold, and other heavy resistant minerals, although the richest strips appear to be in California. At Aptos, Santa Cruz County, an occurrence in the shape of an irregular crescent 50 feet wide extending for 200 feet along the foot of a detrital cliff carries layers of black sand, from the thickness of cardboard to 6 inches, which are separated by strata of lean sand throughout a profile of several hundred feet. The sand is said to average 16 per cent titanium dioxide and to yield a concentrate carrying 40 per cent of this constituent. Another extensive concentration is found south of Redondo, in Los Angeles County. This deposit consists of a lens-shaped body of the black sands from 14 inches to 8 feet in thickness, overlaid by gray and white quartz sand. The sands, as worked, contain 20 per cent titaniferous iron ore and magnetite mixed with silica, olivine, epidote, garnet, and zirconium silicate. Ilmenite has been produced sporadically from both these deposits.

Concentrations of ilmenite sands derived from nelsonite are known along stream courses in Virginia. Occurrences of minor importance have been described in Georgia, Texas, Maryland, Oklahoma, Missouri, Montana, and Washington.

AFRICA. Deposits of heavy black sands occur along the beach of Senegal, West Africa, from Rufisque to the north of the mouth of the Saloun River and near the mouth of the Casamance River.[42] The sands, which are of unknown but probably marine origin, are transported by high tides, particularly during the winter season. Zircon and quartz are mixed with the titanium-bearing component which, although generally called ilmenite, contains 55 to 60 per cent titanic oxide. Because of this chemical composition it is not a true ilmenite. Grains of quartz are coarser than those of zircon so that screening offers a partial separation, and screening combined with magnetic treatment effects complete separation.

Later investigations indicated that the titanium is present as the mineral arizonite. These ores contain a relatively large proportion of chromium which has replaced ferric iron. The deposits constitute a large potential source of ore containing around 52 per cent titanium dioxide. The chromium content by the conventional methods of manufacture, however, tends to give a discolored pigment.

Ilmenite sands containing 37 per cent titanium dioxide occur along the Gulf of Guinea, Ivory Coast. Shaking screens yielded a concentrate containing 44.3 per cent titanium dioxide, 14.2 per cent silica, and 12.4 per cent zirconium oxide, and further magnetic treatment raised the titanium dioxide to 52 per cent and eliminated most of the other constituents. Other deposits have been reported in South Africa.[43] The black sands of Egypt are amenable to selective flotation.[44] Ilmenite and magnetite were removed by sodium sulforicinate with oleic acid in an alkaline solution. Concentrations of heavy black sands have also been reported in Gambia, on the Gold Coast, in Nigeria and South Rhodesia, and on the island of Madagascar.

LATIN AMERICA. Large beach deposits of ilmenite, mixed with monazite, zircon, garnet, and quartz sand occur along the southeast coast of Brazil.[45] The principal beaches are located at Guarapary and Boa Vista, in the State of Espirito Santo, in the vicinity of Prando, in the State of Bahia, and just south of Barra do Itabapoana, in the State of Rio de Janeiro. By a system of concentration and magnetic separation, an ilmenite product may be obtained containing around 50 per cent titanium dioxide. The deposits at Espirito Santo have been developed and worked sporadically. There is a very large quantity of available ilmenite on the Brazilian coast. According to Abreu,[46] these sands were derived from archean granites and gneisses. In places the titanium dioxide content of the sands may be as high as 43.6 per cent. A concentrate containing 71.6 per cent ilmenite, 6.0 per cent monazite, and 12.9 per cent zircon may be obtained by water tables and magnetic separation.

ARGENTINA. Considerable quantities of beach sands are found, said to contain 24.7 per cent ilmenite, 29.2 per cent magnetic iron sand, and 27.9 per cent ferruginous black sand, not magnetic. The principal deposits extend southward from Meconchea through the Straits of Magellan. Similar occurrences have been reported in Guatemala and Mexico.

EUROPE. In Europe there is a workable deposit of ilmenite sands in the district of Castelo Branco, Portugal, and production from this area has amounted to a few hundred tons a year. Other occurrences have been reported in Italy, Sweden, Switzerland, Yugoslavia, and Czechoslovakia.

FLOTATION. Relatively recently there has been developed a new type of collector which is particularly applicable to flotation of ilmenite and other minerals whose suspensoids in water are negative.[47]

Characteristic examples of this type of reagent are the heavily loaded quaternary ammonium salts and cetyl pyridium bromide which give a positively charged surface-acting ion in aqueous solutions. The hydrocarbon mineral-oiling end of the molecule is the positive ion (micelle). Such substances are now generally referred to as cationic agents, in contrast to xanthates and the fatty acids which have the hydrocarbon chain in the anion and are known as anionic oilers. A concentration of iron and titanium compounds may be obtained by subjecting a pulp of the sand to froth flotation in the presence of wood creosote, the sodium salt of a sulfonated mineral oil, and oleic acid or a fatty acid soap.[48] Pickens [49] obtained an ilmenite concentrate containing 52.81 per cent titanium dioxide which represented a recovery of 56.35 per cent. The ore was ground with 1.5 pounds sodium hydroxide per ton, deslimed by decantation, and given a rough silicate float at 35 per cent solids by conditioning for 5 seconds and floating for 2 minutes with 0.06 pound per ton pine oil and 0.2 pound of the reaction product of thiourea and beta chloroethyl oleate, a reagent of cationic type. This concentrate was then floated.

Rutile

The largest known deposits of rutile are in Nelson County, Virginia, at Kragero, Norway, and at St. Urbain, Quebec, Canada. Other occurrences of importance are in the provinces of Queensland and South Australia, Australia, in the island of Madagascar, in Brazil, and in Arkansas and Florida.

UNITED STATES. According to Hess and Gillson,[50] the rutile deposit at Roseland, Virginia, is a broad pegmatite replacement of a peculiar aplite which was intruded into granite gneiss. This aplite, composed of sodic plagioclase interfingered with a small proportion of potash feldspar, was broken with innumerable cracks and some rather large faults. Magmatic solutions rising along these openings deposited grains of clinozoisite, blue quartz, pyroxene, hornblende, ilmenite, and rutile by replacement of the aplite. In areas highly disturbed with wide and crossed cracks, the solution penetrated more freely, resulting in more complete replacement, and here rutile formed in masses, some of which weighed several pounds. As in most replacement deposits of this type, the proportion of minerals varies from place to place.

Both rutile and ilmenite in comparatively small grains follow the cracks through the pegmatites, although the ilmenite is found mostly

with the hypersthene and hornblende. Considerable proportions of white apatite are also present. This rock, which averages 4 to 5 per cent each of rutile and ilmenite, has been mined since the turn of the century. It is first crushed and separated on a shaking table to yield a concentrate which in the long run seems to afford approximately equal quantities of the two minerals. The ilmenite is removed from the ore concentrate by a Wilfley magnetic separator, yielding a rutile fraction containing 92.5 to 98.0 per cent titanic oxide. Areas of badly weathered pegmatites between Peers and Johnson's Spring, in Goochland County, and near Gouldin, in Hanover County, carrying dull-red rutile intergrown with ilmenite and white and green apatite, have been prospected, but the deposits proved too small for profitable development.

At Magnet Cove, Arkansas, titanium dioxide in the form of rutile, octahedrite, and brookite occur in connection with nephelite syenite. The rutile occurs as a primary or secondary mineral in an igneous massif. The heavy minerals are concentrated by gravity methods and this concentrate is floated and jigged. After magnetic separation, a product containing 95 per cent titanium dioxide is obtained.[51]

The mineral concentrates from the black sands of east Florida, Mineral City workings, contain 6 per cent rutile. Other occurrences have been reported on Shooting Creek, North Carolina, in east Alabama, Georgia, New Jersey, Pennsylvania, South Carolina, South Dakota, and Washington.

NORWAY. The important deposit at Kragero, in southern Norway, carries 10 to 15 per cent rutile in association with a moderately acid plagioclase known as kragerite. Productive rock occurs as streaks or stripes in foliated granite, with an enormous dike of granite-pegmatite on one side and of olivine-hyperite with amphibolite on the other, both of which are traversed by aplite-rutile veins. The rock mass yields a black rutile concentrate containing 97 per cent titanium dioxide and abnormally high proportions of chromium and vanadium. The most prominent megascopic constituents of the ore are light-gray and pinkish feldspars, and some rutile with a little quartz. The rutile grains rarely exceed 1 millimeter in diameter, and many are less than ½ millimeter.

CANADA. One of the ilmenite occurrences located 2 miles west of the village of St. Urbain,[52] Quebec, Canada, contains enough admixed rutile to make it of possible importance as a source of this ore alone. Rutile, accompanied with sapphirine and ilmenite in-

closed in granular masses of ilmenite, has been intruded into anorthosite. The ore-bearing rock, of a brownish-black color, consists of granular ilmenite sprinkled with grains of orange-red rutile, feldspar like that in the enclosing anorthosite, biotite, sapphirine, and spinel. Microscopically, the ilmenite forms a background in which the other minerals lie. The size of the rutile particles ranges from mere specks to grains 3.5 millimeters in diameter and averages 0.6 millimeter. Rutile content of the rock varies from 8 to 20 per cent.

LATIN AMERICA. Brazil's rutile resources [53] are in the states of Goyaz and Minas Geraes. Production from the latter state ordinarily contains ilmenite, and the ore accordingly analyzes only 70 to 85 per cent titanium dioxide. That from Goyaz is of a better quality, however, and runs up to 95 per cent or even more. These deposits have been worked on a limited scale for a number of years. At Bon Jardin [54] the rutile occurs contaminated with oxides of iron, most of which are in the form of ilmenite, but after crushing the crude material to a particle size of 0.15 to 0.20 millimeter in diameter, magnetic separation gives a high-grade rutile concentrate. Samples from British Guiana showed 95 per cent titanium dioxide. Occurrences of minor importance have been reported in Mexico and Guatemala.

GREENLAND. Rutile and titanite occur in the sands of East Greenland.[55]

AFRICA. Rutile is known to occur at a number of localities in Africa. The sands of Yaounde River, Cameroons,[56] contain commercial quantities, and a small production of rutile has been reported in recent years. It is also found in the former German colonies,[57] and the sands of Souf, south of Constantine, Algeria,[58] contain a considerable proportion of this mineral. Occurrences have also been reported in the French Congo, Belgian Congo, British West Africa, and South Africa.

MADAGASCAR. Rutile is found in some abundance in Madagascar.[59] The most important occurrence is in the mica schists to the west of Ambstrofinandrahana and north of the Matsiatra River. It occurs as large crystals in the enclosing rocks, and small quantities of the loose mineral have accumulated in placers as a result of weathering. Ore from this deposit was used during the first World War for the manufacture of titanium tetrachloride to be used as a screening agent.

UNION OF SOVIET SOCIALIST REPUBLICS. Rutile occurs in the central Kyzyl-Kum.[60]

TABLE 1

Analyses of Ilmenite Ores in Percentages

Region groupings: **UNITED STATES** — Virginia (Piney River, Roseland), New York, California, Florida, Georgia · **CANADA** — Ivry, Bourget · **BRAZIL** · **ASIA** — India (Travancore: Manavalakurichi, Quilon, and others), Molay States, Sirolit Settlement · **EUROPE** — Norway, U.S.S.R., Portugal · **AFRICA** — Senegal, Sierra Leone

Chemical Constituent	Piney River	Piney River	Piney River	Roseland	New York	California	Florida	Georgia	Ivry	Ivry	Bourget	Brazil	Brazil	Manavalakurichi	Quilon	India	India	Molay States	Molay States	Sirolit Settlement	Norway	Norway	Norway	U.S.S.R.	Portugal	Portugal	Senegal	Senegal	Sierra Leone
TiO_2	44.3	43.7	45.6	51.4	44.3	48.2	52.0	34.4	32.4	42.5	22.4	61.9	48.3	54.3	53.6	60.3	60.0	51.7	54.0	55.3	37.0	43.9	42.3	44.0	52.2	42.1	54.7	56.0	42.3
FeO	35.9	37.6	36.8	37.9	36.7	39.1		11.3		31.1	36.9	1.9	32.4	26.0	26.7	9.7	11.8	38.5		26.7	32.6	36.0	33.9	31.4	42.1		7.3	14.2	28.0
Fe_2O_3	13.8	13.2	15.8	1.6	4.4	10.4		7.8		20.7	31.2	30.2	16.6	15.5	14.2	24.8	21.9	3.77	5.76	13.0	23.0	11.1	11.1	16.9			30.3	28.2	25.0
SiO_2	2.0	1.7	1.1	4.6	3.2	1.4		43.1	3.9	0.88	1.0	1.4	1.4	1.40	0.90	1.4		1.00	0.50	0.7	0.62	3.28	3.50	18.4			1.30	0.9	
Al_2O_3	1.21	0.8	0.7	0.55	0.19	0.2		none	1.7	1.05	6.01	0.25	0.3	1.10	1.11	1.0			1.56	0.5	0.59	0.85	1.8				0.50		
P_2O_5	1.01	0.8	Trace	0.17	0.07			0.18		Trace	0.93			0.26	0.54	0.17		0.09		0.19	0.06	0.12	0.01	0.15	0.27	0.29	0.14	0.15	
ZrO_2	0.55				0.006	0.05		0.12				0.07	0.1	2.18	1.00	0.60	0.2			0.10	none	1.09	0.03		0.03		2.37		
MgO	0.07	1.0	0.5	2.35	0.80	0.6		none	1.0	2.0	1.50	0.3	0.1	0.85	1.01	0.65		none		0.02	3.04	3.69	1.60	2.76	0.03		1.90		
MnO	0.52	0.3	0.12	0.70	0.35	0.1		1.89		0.04		0.1	0.6	0.40	0.48	0.40		0.21		0.70	0.25	0.33	0.35	0.72	5.00		1.32	0.20	
CaO	0.15	0.3	0.10	0.59	1.0	0.1		none	3.2	0.1	0.55	0.1	0.1	0.08	0.15	0.15	0.5	3.15	3.97	0.50	0.10	0.18	0.20		0.09		0.10		
V_2O_5	0.16	0.09	0.27	0.07	0.24	0.05				0.36		0.2	0.06	0.20	0.03	0.26		0.04		0.07	0.48	0.20	0.40	0.05			0.27		
Cr_2O_3	0.27	0.04	0.10	none	0.001	0.03				0.15		0.1	0.5	0.07	0.09	0.14		0.02		0.03	0.07	0.03	0.007				0.23	0.32	0.38
SnO_2					0.001	0.001				0.001		0.001	0.003	0.06	0.01	0.01				0.25		0.05	0.001						Trace
CuO	0.00005	0.001	0.001	0.02	0.0004	0.005								0.01	0.005									0.60					
ThO_2																					0.08			0.60					
CoO	0.02			0.01	0.002			0.28						0.08	0.02	0.01					0.02								
CeO_2		0.005						0.53						0.02	0.01						0.01								
PbO	0.0005		0.005			0.005								0.005		0.004					0.01		0.001						
WO_3			0.05											0.04	0.02						0.001		0.001						
NiO					0.005	0.005								0.006	0.002	0.004					0.02		0.02						
Au		0.005	0.001											0.02	0.05	0.02													
Pt		0.05												0.1	0.08														
Cb	0.0002		0.0005	0.0005	0.002	0.005															0.005		0.005						

22

The Soviet government was reported in 1937 and 1938 to be actively mining sphene from a large deposit on the Kola Peninsula, apparently for making titanium pigment, although efforts to develop markets for Canadian sphene were unsuccessful.[61]

Residues from Bauxites

Coghill [62] has pointed out that bauxite is a potential source of titanium. In 1928 the waste sludge discharged daily at the East St. Louis plant of the Aluminum Company of America contained more than 75,000 pounds of titanium dioxide. Residues from the Bayer process of purifying bauxite,[63] or from digestion with sulfuric acid, yielded rutile and ilmenite by concentration on tables.[64] A sample containing 3.2 per cent titanium dioxide, after tabling, regrinding, and retabling was increased to 39.7 per cent.[65]

Analyses of Ores

ILMENITE. Based on the titanium dioxide content, ilmenite ores may be arranged roughly into four main groups, according to locality: Canada, with about 30 per cent titanium dioxide; Virginia, New York, Norway, and Union of Soviet Socialist Republics, with about 43 per cent of the dioxide; Florida, Virginia (Roseland), Maravalakurichi, Travancore, India, Malay States, and Portugal, around 52 per cent titanium dioxide; Quilon, Travancore, India, Brazil, and Senegal, West Africa, carrying approximately 60 per cent. Both the Quilon and Senegal ores usually classed as ilmenite contain a large proportion of the mineral arizonite.

The analyses of regular ilmenite concentrates from the more important deposits as collected from many but reliable sources are given in Table 1.

RUTILE. Rutile concentrates, as marketed, usually average 94 to 98 per cent titanium dioxide. Representative analyses of samples from Australia showed 94 per cent titanium dioxide, from Brazil 85 to 95 per cent, from Cameroon 90 to 95 per cent, from Norway 90 to 93 per cent, and from Southwest Africa 94 to 98 per cent. A sample of rutile from Nelson County, Virginia, contained 99.28 per cent titanium dioxide, 0.40 per cent ferrous oxide, 0.28 per cent vanadium pentoxide, and 0.04 per cent chromic oxide. Another sample from Amherst County showed 99.7 per cent titanium dioxide, 0.20 per cent vanadium pentoxide, and 0.07 per cent chromium trioxide.

Chapter 5

PRODUCTION AND IMPORTS OF TITANIUM-
BEARING ORES

Production of Ilmenite

The black sands of the native state of Travancore, India, the titaniferous magnetites of New York State and of the Union of Soviet Socialist Republics, and the lode deposits of southern Norway have supplied much the larger part of the world's production of ilmenite, although Virginia, Florida, and North Carolina, Canada, Japan, Australia, Africa, and Malaya have accounted for smaller but appreciable amounts.[1] Minor tonnages have been produced in Brazil, Egypt, Portugal, and Madagascar.

INDIA. The Travancore deposits were first worked for monazite in 1911, but not until 1922 was ilmenite saved, when production was 406 tons. Except for a slight recession in 1929, production steadily increased to around 250,000 tons in 1940. As a result of war conditions and lack of shipping space, production decreased to 2000 tons in 1942, but again increased to around 225,000 tons in 1946. These beaches have supplied more than 2,000,000 tons of concentrate and are expected to continue on a large scale for years to come. There seems to be some question, however, whether the production can be expanded continuously, so efforts have been made to develop other stretches of beach around the southern point of India and in Ceylon.

UNITED STATES. Significant production of ilmenite in the United States began in 1922 along the east coast of Florida. Until 1926 the output amounted to around 5000 tons annually, but it decreased to 3500 tons in 1927 to 918 tons in 1928. Although official figures are not available, indications are that production remained below 1000 tons a year until 1935 when there was a substantial increase in output from Virginia to supply the requirements of a pigment plant at Piney River. In 1945 the expanded development, together with the pigment plant, was sold by the Virginia Chemical

Company to the Calco Chemical Company, a division of the American Cyanamid Company. Production held around 15,000 tons annually until 1941 when deposits of ilmenite-magnetite in the Adirondack Mountains of New York State were developed to supply the domestic requirements of ore formerly imported from India but cut off temporarily by war conditions. Output expanded rapidly. In 1944 about 200,000 tons of concentrate were obtained from 1,000,000 tons of ore mined, and in 1947 the production amounted to around 300,000 tons of ilmenite concentrate. Although initial development was by the National Lead Company, a 25 per cent interest was granted E. I. du Pont de Nemours and Company in 1944.

Late in December, 1947, E. I. du Pont de Nemours and Company announced a long-term lease of ilmenite-bearing land from the State of Florida, located in the north central area of the State, and large-scale production began in 1948.

Ilmenite deposits at Finley, Caldwell County, North Carolina, were developed in 1942 by the Yadkin Valley Ilmenite Company, a subsidiary of the Glidden Company, and in 1944 the output amounted to approximately 15,000 tons. In 1946 the production from this area reached 17,102 tons of ore averaging 52.4 per cent of titanium dioxide.

The total production of ilmenite in the United States reached 308,516 tons in 1945, decreased to 282,447 tons in 1946, but reached a maximum of 336,533 tons in 1947.

Domestic production was expanded very much during the war years, since imports of ore practically ceased because of lack of shipping space. Indications are that the high domestic production will continue, but profitable disposal of iron ore by-product may prove a determining factor. It should also be noted that the beaches of India can supply large quantities of the ore at a low price, which before the war was about $5 per ton for ore and $5 for freight delivered at New York.

NORWAY. From 1920 to 1931 the production of ilmenite from Norwegian deposits varied from approximately 3000 to 8000 tons a year, but showed a substantial increase to 13,841 tons in 1932 and 67,194 tons in 1936. In 1937 the output decreased to 51,516 tons, due in part to suspension of shipments to the United States. The reason was given that these ores tended to give pigments of poor chalking resistance and poor color. From 1938 to the close of

World War II the entire production of slightly more than 60,000 tons annually went to Germany. In 1946 production was resumed by the National Lead Company, and 30,026 tons were shipped to the United States in 1947. Production has since been expanded more than 50 per cent.

UNION OF SOVIET SOCIALIST REPUBLICS. An appreciable amount of titanium ore has been produced in the Soviet Union for a number of years, but definite figures are not available. The Soviet government was reported to be actively engaged in mining sphene on the Kola Peninsula in 1937 and 1938.

MALAYA. Before World War II, ilmenite concentrate produced from the "amang" or waste black sand obtained as a by-product in working the placer cassiterite deposits in the Malay Peninsula was shipped to England, Holland, and Japan in steadily increasing quantities. In 1936 the output amounted to 10,470 tons; it increased to 11,098 tons in 1938, but fell to 2555 tons in 1940, evidently because of war conditions. Similar operations have been reported on the island of Billiton.

CANADA. After holding around 2000 to 5000 tons for many years, the production of ilmenite in Canada increased to 65,437 tons in 1943 but decreased to 32,580 tons in 1944 and to 6981 tons in 1945. In 1947, production amounted to 7122 tons.

BRAZIL. Although the production of ilmenite in Brazil has been small and erratic, it increased to 5511 tons in 1944 and to 10,508 tons in 1945. It practically ceased, however, in 1946 and 1947.

AFRICA. Senegal, West Africa, produced 8436 tons of ilmenite in 1938, 4840 tons in 1942, and 770 tons in 1943. Indications are that production since 1943 has been insignificant.

HUNGARY. Before the war, titanium compounds were reported to have been obtained from bauxite residues.

WORLD PRODUCTION. The estimated world production of ilmenite, outside of the Soviet Union, was 5000 tons in 1920, 45,000 tons in 1930, 300,000 tons in 1938, approximately 550,000 tons in 1946, and around 600,000 tons in 1947.

COMPOSITION OF ORES. The titanium dioxide content ranged from 44 per cent in the domestic and Norwegian ore up to 59 per cent in the Indian product. The Quilon product normally contains

approximately 59 per cent titanium dioxide, and the remainder of the Travancore ores run from 52 to 54 per cent of this constituent.

Production of Rutile

Virginia, Arkansas, and Florida, in the United States; Australia; Brazil; Norway; and Cameroon in Africa are the leading producers of rutile.

UNITED STATES. The principal rutile-producing areas are at Roseland, Virginia, near Hot Springs, Arkansas, and along the beach near Jacksonville, Florida. The estimated total production of rutile concentrate amounted to 45 tons in 1925, 500 tons in 1935, and 2000 tons in 1938. Production expanded to 6279 tons in 1944, 7452 tons in 1946, and 8562 tons in 1947.

AUSTRALIA. Rutile production in Australia was expanded greatly during the war years, from 465 tons in 1938 to 4694 tons in 1941, and to 8843 tons in 1945. Most of the ore was shipped to the United States, since ships returning from Australia had available space. Production amounted to 4377 tons in 1946 and 7460 tons in 1947.

NORWAY. From 1926 to 1933 the production of rutile in Norway amounted to about 50 tons a year, and since 1934 has been around 150 tons annually.

BRAZIL. The production of rutile in Brazil increased steadily from 35 tons in 1932 to 500 tons in 1940, to 4900 tons in 1942 and 1943, decreased to 1564 tons in 1944, to 160 tons in 1945, and ceased in 1947.

AFRICA. Production from Cameroon increased from 45 tons in 1935 to 503 tons in 1940, to 2153 tons in 1942, and to 2902 tons in 1944. Production in 1946 and in 1947 was negligible.

WORLD PRODUCTION. The estimated world production of rutile increased steadily from 200 tons in 1930 to 1000 tons in 1935, 5421 tons in 1940, 14,750 tons in 1942, and 19,588 tons in 1944, but it decreased to around 16,000 tons in 1947.

COMPOSITION OF ORES. The rutile concentrates, as shipped, usually contain from 93 to 94 per cent titanium dioxide, although values may range from 90 to 99 per cent.

Political Considerations Governing Production

The British government and commercial concerns control the extensive Indian and Malayan reserves, but the ore is sold in the world markets at what appears to be a nominal price.

Available deposits in the United States are probably on a par with those in Norway. The latter are controlled, however, by the National Lead Company of New York. In French and Soviet Union territory none but native companies may operate, and exports are carefully watched. No duties are levied in the United States on imports of titanium ores.

Imports of Ilmenite

Prior to World War II, the domestic production of ilmenite ores supplied only a very small part of the demand that had developed from the expanding use of titanium in the pigment, metallurgical, electrical, ceramic, and other industries.

In 1928, the first year for which accurate figures are available, imports amounted to 15,685 tons. Imports increased steadily to 287,191 tons in 1939, then decreased to a low of 10,369 tons in 1942 because of lack of shipping space as a result of the war, and again increased steadily to 242,826 tons in 1946.

Prior to World War II, with the exception of 1935 and 1936 when 22,472 and 32,126 tons, respectively, were obtained from Norway, India supplied practically the entire amount. Imports from Canada ranged from around 2000 to 6000 tons for a number of years prior to 1943, amounted to 65,437 tons in 1943, and 32,580 tons in 1944, but dropped back to the more normal value of 6981 tons in 1945. For a number of years ilmenite to the amount of a few thousand tons has been imported annually from Brazil; in 1945 this amounted to 10,508 tons. In 1944, Ceylon supplied 4648 tons. Imports from Norway, which were resumed in 1945, amounted to 9895 tons that year and to 30,026 tons in 1947.

Imports of Rutile

Imports of rutile amounted to 79 tons in 1933 and 364 tons in 1938, increased rapidly during the war years to 9635 tons in 1943, and decreased to 3699 tons in 1944 and to 3304 tons in 1945. Practically all this amount came from Brazil and Australia.

The imported rutile, together with the much larger domestic production during the war years, was used largely in coating welding rods for building welded ships, tanks, guns, and other war equipment. This method of construction proved much faster than riveting. Since the war this practice has been transferred to the production of civilian goods, and as a consequence the consumption of rutile has remained high.

Chapter 6

THE CHEMISTRY OF ELEMENTAL TITANIUM
AND ITS OXIDES

Elemental Titanium

PRODUCTION. The production of pure elemental titanium is fraught with many difficulties because of its high melting point and strong affinity for nitrogen and carbon as well as for oxygen. Although many attempts were made by the earlier investigators with varying degrees of success, probably the first to prepare the pure metal was Hunter [1] in 1910. Previous attempts to prepare the metal from its compounds usually resulted in nitrides, carbides, or cyanonitrides which, because of their metallic luster and appearance, were often mistaken for the element. Among the pioneer investigators were such well-known scientists as Klaproth,[2] Berzelius,[3] Wollaston,[4] Wohler,[5] and Deville.[6] In 1887 Nilson and Petersson [7] obtained a product of 94.7 per cent purity by reducing titanium tetrachloride with sodium in an airtight steel cylinder. The chief impurity was oxygen, and since this was considered to be combined as titanium monoxide, the sample contained only 78.9 per cent metallic titanium. Perhaps the nearest approach to the pure element, prior to the work of Hunter, was that of Moissan [8] who reduced titanium dioxide with carbon in a lime crucible at the temperature of a powerful electric arc. The primary product contained 5 per cent carbon, but by reheating with added titanium dioxide the amount was reduced to 2 per cent. Since the carbon was probably in chemical combination, the material was far from pure titanium metal. Two museum samples [9] examined some years later proved to be quite pure, but contained titanium carbide and iron as cell walls surrounding pure titanium crystals. Huppertz [10] is reported to have made a high-grade product, relatively free from oxygen and nitrogen, by an electrolytic process employing titanium dioxide in a calcium chloride electrolyte. The cell was a strontium metal furnace.

In his earlier work, Hunter [11] attempted to reduce sodium titanofluoride with potassium in an iron cylinder, but the best samples contained only 73.2 per cent titanium. Potassium and barium tita-

nofluorides gave no better results. Reduction of the oxides with carbon, after the method of Moissan, yielded a product containing 4.6 per cent carbon. Finally, following the method of Nilson and Petersson, and exercising extraordinary care to exclude air from the apparatus, metallic titanium practically free from impurities was obtained. The titanium tetrachloride, prepared by chlorinating titanium carbide, was carefully purified by shaking with mercury and sodium amalgam followed by redistillation in an atmosphere of nitrogen to give a colorless constant boiling liquid. This purified titanium tetrachloride, together with the theoretical amount of sodium, was transferred to a steel bomb of 1000 ml. capacity, capable of withstanding an internal pressure of 80,000 pounds. A typical charge consisted of 500 g. titanium tetrachloride and 246 g. metallic sodium. On heating the system to dull redness, the reaction took place with explosive violence and was almost instantaneous. The cooled and washed product consisted of small metallic beads, together with a minor proportion of the same material in the powder form. Two analyses of the beads gave 99.9 and 100.2 per cent of titanium, and no trace of iron or sodium was found. Ninety per cent of the titanium in the original charge was recovered as metal. These results were confirmed by Lely and Hamburger,[12] who reduced the tetrachloride with sodium in a steel bomb and fused the metal in an electric vacuum furnace. In a modification of this process, titanium tetrachloride was heated in a closed vessel with sodium, in the presence of a minor proportion of titanium dioxide or titanium nitride or cyanonitride.[13] The pure metal was produced in Germany by heating the tetrachloride with sodium at 800° C. under a flux of sodium chloride and potassium chloride.[14]

An amorphous product of 85.7 per cent purity was prepared by reducing potassium titanofluoride with sodium.[15] After pressing the metal into sticks and fusing it in a vacuum furnace, the titanium content was found to be 97.5 per cent. According to Vaurnasos,[16] titanium tetrachloride is hard to reduce to the metal with potassium. A lower chloride formed, but on long heating the metal was obtained. Elemental titanium was also obtained by introducing the tetrachloride in vapor form into a bath of fused potassium chloride maintained at 700° to 900° C. and covered with a molten layer of an alkali metal [17] in an inert atmosphere. Kroll [18] reduced titanium tetrachloride with pure magnesium in a molybdenum-lined, electrically heated crucible at 1000° C. in an atmosphere of argon. The metal was separated from excess magnesium salts by leaching and acid treatment; no alloy of the two metals formed. The powdered

titanium was compressed into bars and melted in a special electric vacuum apparatus. After this treatment, the product was easily hot-rolled and a strip less than one millimeter thick could be bent cold without fracture.

Attempts were made by Ruff and Brintzinger [19] to reduce oxides of titanium with sodium, calcium, and sodium-calcium alloy in a wrought-iron bomb. While sodium reduced the oxides at 900° to 950° C. rather ineffectively, calcium was more effective, and a 30 per cent sodium-calcium alloy gave best results, yielding at this temperature 82 to 88 per cent recovery. Titanium dioxide was reduced to the metal by heating with calcium and a powdered, fused, 75 to 25 mixture of calcium chloride and barium chloride in an electric furnace in an atmosphere of argon at temperatures up to 750° C. [20] After a second reduction the product was ground and treated with water and strong hydrochloric acid. All efforts to remove the small proportion of lower oxides failed.

By carrying out the aluminothermic reaction in a hot electric furnace, Lohmann [21] obtained the pure metal. Merle [22] carried out the reaction between purified powders of titanium oxide and aluminum in a centrifuge, to effect better separation and recovery. Iwase and Nasu [23] found that only after mixing titanium dioxide with lampblack did reduction with atomic hydrogen and formation of carbide take place. Pure metal was produced only with difficulty. The dioxide was not reduced directly with atomic hydrogen.

Stahler and Bachman [24] obtained metallic titanium of 94 per cent purity by distilling the dichloride in an atmosphere of hydrogen at 1100° C. The tetrachloride mixed with hydrogen was reduced on passing through an iron tube at 900° C., but the inner walls of the tube combined with the liberated titanium to form an alloy. [25]

According to Van Arkel and De Boer, [26] titanium prepared by reducing the tetrachloride with sodium always contains traces of oxides and nitrides, and electrolysis of double fluorides produces no better result. These workers found that metal could be produced in very pure form by heating in an evacuated vessel a compound which dissociates into the metal and a gas at a temperature below the melting point of the metal. Titanium tetraiodide fulfills these requirements. Its vapors were heated in a glass chamber, freed of air, at 650° C., and a layer of titanium was deposited on a filament (tungsten) located in the upper part of the vessel and heated electrically at 2000° C. Iodine was liberated and recombined with impure titanium powder placed on the bottom of the glass chamber so that the process proceeded until the supply of anode titanium was

used up. By this method the metal was not fused and did not come in contact with impurities. The iodide gave better results than the tetrachloride, since it dissociates at a lower temperature. Titanium produced in this manner is of the highest degree of purity.

In a survey of the entire field, Fast[27] prepared titanium in a relatively impure form by the reduction at 1000° C. of potassium titanofluoride with 1 per cent excess sodium, or of sodium titanofluoride with sodium in 10 per cent excess. Fluorides were extracted from the reaction product, the mass was boiled with strong sodium hydroxide solution, and the surface oxidation products were removed by treatment with dilute hydrochloric acid. Pure samples were obtained by the reduction of the tetrachloride with sodium at 700° to 800° C., or at even lower temperatures, in the presence of potassium chlorate to initiate the reaction.

Pure titanium was also obtained by the thermal decomposition of the iodide. The metal reacted with iodine vapor at room temperature and formed the dark-red vapor of the tetraiodide at 200° C., which was decomposed by a tungsten wire heated to at least 1100° C. to effect deposition of the titanium. The nature of the deposit depended both upon the characteristic of the core and the temperature of the filament, but in general it was smoother at 1300° than at 1100° C. Deposition increased as the temperature of the vapor inside the closed vessel rose to 150° C., but at 200° C. the reaction, $TiI_4 + Ti \rightleftarrows 2TiI_2$, became a factor. At 250° C. the reaction, $2TiI_2 \rightleftarrows Ti + TiI_4$, became important. Deposition became slight at 300° C. and ceased at 350° C. All iodine was believed to have been converted to TiI_3.

The metal may be produced on a commercial scale by reducing the finely divided dioxide with natural gas.[28] It was first produced in large quantities by reducing the tetrachloride with magnesium in an atmosphere of argon or helium.[29] Purified titanium tetrachloride was dripped onto molten magnesium at 700° C., the resulting mixture was leached with dilute hydrochloric acid, and the powder residue was pressed into shape at 1000° C. in vacuum. After considering virtually every process that had been proposed for the production of ductile titanium, Dean[30] and others concluded that this method of Kroll was the most practical for large-scale operation and developed a number of modifications. The modified method was employed by the United States Bureau of Mines to produce titanium metal on the pilot-plant scale by reduction of the tetrachloride with magnesium. After critically studying a number of methods, Hanna and Wormer[31] likewise concluded that a modi-

fication of the Kroll process was best suited for producing titanium needed in compounding getting mixtures. The tetrachloride was reduced with magnesium at 800° to 950° C. to produce a product of not less than 98 per cent purity. Three methods were used by the Germans during World War II to produce the metal.[32] Potassium chloride, sodium chloride, and metallic sodium were heated in a covered iron pot to 800° C., and titanium tetrachloride was introduced, with stirring. The reaction product was cooled, re-
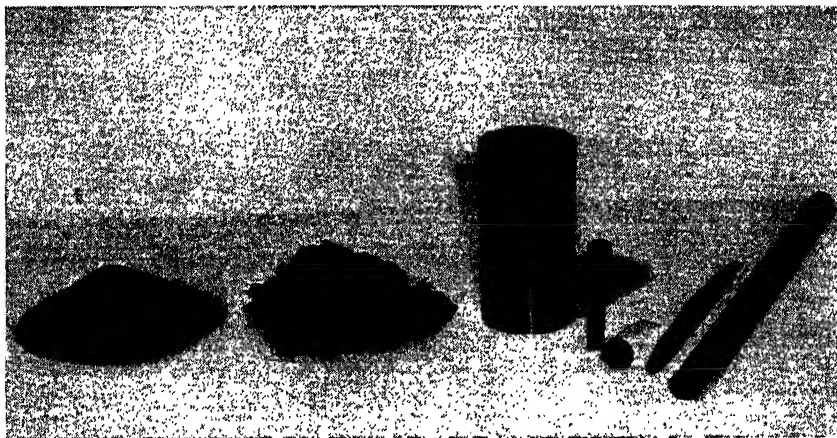
Figure 3. Ilmenite ore, sponge form titanium metal, titanium ingot, and small articles fabricated from metallic titanium

(Courtesy E. I. du Pont de Nemours and Company)

moved from the pot, and treated with hydrochloric acid to separate the titanium as a residue.   By another method, purified hydrogen was passed through a vaporizer containing titanic bromide into a quartz tube heated by tungsten wires at 1200° to 1400° C. As titanium built up on the wires, an increase in current was necessary to maintain decomposition temperature. According to a third process, titanium dioxide was heated with calcium hydride in a tube furnace made of molybdenum. The reaction mass was contained in shallow boats pushed into the tube heated at 700° C. Reaction was complete in ½ minute, and the boats were discharged at the opposite end of the tube. This product was treated with boiling formic acid, which dissolved the calcium oxide, leaving pure titanium as a gray powder. A similar process was employed by Alexander,[33] who recommended that the powder be packed in an inert gas such as argon or helium, to prevent oxidation.

On September 14, 1948, E. I. du Pont de Nemours and Company announced the commercial production of titanium metal in sponge and ingot forms of 99.5 per cent purity.[34]   Initial output was 100 pounds daily and the initial price was $5 a pound.

PROPERTIES.   Titanium falls in Group IV of the periodic classification of the elements, according to Mendeleeff, and heads Subgroup A, which also includes zirconium, hafnium, and thorium. Titanium forms salts which hydrolyze readily in solution, on heating or dilution, to yield a precipitate of hydrous oxide, and this property is taken advantage of in the commercial manufacture of titanium pigments.[35]

Analogous salts of the other members of the group show increasing stability in solution with higher atomic weights, and metallic properties become more pronounced in the same direction. Similarly, the amphoteric nature of the dioxides, which is very pronounced with titanium, ends with zirconium, and thorium oxide exhibits basic properties only. The metallic (basic) role of titanium is exhibited in such compounds as sulfates, chlorides, and phosphates, while the nonmetallic (acidic) characteristic appears in a long series of titanates and titanofluorides or fluotitanates.

In addition to the characteristic valence of four, divalent, trivalent, and pentavalent compounds are well known and others have been reported. Quadrivalent titanium is isomorphous [36] with silica in garnet, hornblende, enigmatite, mica, tourmaline, and olivine, with zirconium in the astrophyllite group of minerals, and with columbium in lavenite. Trivalent titanium is isomorphous with aluminum in titanaugite and with the rare earths in the titanite group.

Titanium is one of the few elements that can be made to "burn," that is, react with incandescence in an atmosphere of nitrogen.[37] The combination takes place with great readiness and begins at a temperature of around 800° C. The metal ignites in air at 1200° C., in oxygen at 610 ° C., and burns with incandescence. It decomposes steam at red heat, 700° to 800° C., to form the oxide and hydrogen. Titanium is attacked rapidly by concentrated sulfuric and hydrochloric acids, and slowly by dilute sulfuric acid, but concentrated and dilute nitric acids have no appreciable effect. It does not tarnish on exposure to laboratory atmosphere or to a salt spray for 30 days. With the halogens it combines directly to form the corresponding tetrahalide; the reaction takes place with fluorine at a temperature slightly above atmospheric, with chlorine at 350° C., with bromine at 360° C., and with iodine at 400° C.[38]

Titanium has an atomic weight of 48.9 and an atomic number of 22. It is a member of the first transitional series of elements, and consequently has variable valence, forms colored ions, and its compounds yield colored aqueous solutions. From repeated mass spectrum analyses, Aston [39] detected five isotypes having atomic weights in order of abundance 48, 46, 47, 50, and 49. The principal line corresponded to isotope with mass number 48, and all the others were faint. Actual proportions of the isotopes [40] were found to be 46, 10.82; 47, 10.56; 48, 100; 49, 7.50; 50, 7.27. The upper limits for other isotypes are: 42, 0.001; 43, 0.01; 44 and 45, 0.002; 51, 52, and 53, 0.0001; and 54, 0.004. From these values the atomic weight was calculated to be 47.88. Walke [41] reported that titanium became very radioactive after bombardment with deuterons, and that the emitted radiations were mainly positrons and hard gamma rays. A radioactive isotope of half life, 41.9 minutes, was produced by alpha particle bombardment. [42] The same effect was produced by bombardment with neutrons. [43] Exposure of titanium 46 to lithium gamma radiation gave a yield of 7.4 per cent of a radioactive isotrope of half life 3 hours. [44]

From X-ray photographs of diffraction in titanium tetrachloride vapor, the atomic radius of titanium [45] was found to be 1.54 Ångstrom units. The paramagnetic character [46] decreased as the valence of the associated ions increased.

The earlier literature on the specific properties of titanium metal reveals many discrepancies which evidently arose from studies of impure samples. Hunter, [47] who was probably the first to prepare and study a practically pure sample, reported it to be a metal resembling steel in appearance, having a specific gravity of 4.50, and a melting point of 1800° to 1850° C. The sample was hard and brittle at ordinary temperatures but could be forged at red heat. Titanium prepared by the iodide method, and probably of even higher purity, was ductile while cold. [48] Rods 7 mm. in diameter were cold drawn to 30 microns, and after heating to 650° C. were hot-rolled into sheets 0.5 mm. thick, and finally into foil 10 microns thick. The cold-worked material had a tensile strength of 126,000 p.s.i., yield strength of 100,000 p.s.i., proportional limit of 72,000 p.s.i., elongation of 4 per cent in 2 inches, density of 4.5, melting point of 1725° C., and hardness Rockwell A of 65. According to Gillett, [49] samples exhibited a tensile strength of 142,000 p.s.i. at 1 per cent elongation. Vacuum annealing at 925° F. resulted in a tensile strength of 56,000 p.s.i. at 12 per cent elongation. More recently a number of investigators, working with large samples of

the pure metal produced on a pilot-plant scale by the modified Kroll process, have studied the physical properties of titanium using standard procedures for pressing compacts, sintering, forging, and annealing.[50] The granular metal was consolidated by pressing into compacts, at a pressure of 50 tons per square inch, and sintering for 16 hours at 950° to 1000° C. in a vacuum of 1×10^{-4} mm. of mercury. The compacts are ductile and malleable, are readily cold-rolled, and may be made into sheets and bars by specific fabricating methods. Annealed samples have a tensile strength of 82,000 p.s.i., with an elongation of 28 per cent, proportional limit of 55,000 p.s.i., hardness of 55 on the Rockwell A scale, density of 4.5, electrical resistivity of 56×10^{-6} ohms per cubic centimeter, and a melting point of 1725° C. The cold-worked material has a tensile strength of 126,000 p.s.i., with 4 per cent elongation, proportional limit of 72,000 p.s.i., and a Rockwell hardness of A 65. These excellent physical properties, together with its noncorrosive characteristic, place titanium high in the list of strong, light metals. The surface of ductile titanium can be hardened by heating the sample in a controlled atmosphere containing small proportions of oxygen or nitrogen. In a specific test, 1.3 mg. of oxygen per square centimeter of surface produced an outside layer having a Rockwell hardness of C 58. The hardening effect appeared to be a solution of TiO in titanium and could be modified by temperature regulation. Samples of the ingot form of titanium metal, after annealing, showed a tensile strength of 80,000 p.s.i., yield strength of 72,000 p.s.i., proportional limit of 38,000 p.s.i., and a hardness of 60 on the Rockwell A scale. Hot-forged rods showed slightly higher values. The metal can be process-annealed by heating in air at 1200° F. for one hour; it is readily forged within the temperature range of 1600° to 1800° F.; machinability is similar to that of austenitic stainless steel; it may be cold- or hot-rolled; and it can be readily spot-welded in an inert atmosphere. Test exposures to a 2200° F. flame for one-half hour indicate that titanium is no more affected than stainless steel. The metal has excellent resistance to sea water, salt spray, and humidified atmosphere. At temperatures above 375° C. it can absorb large quantities of hydrogen, resulting in embrittlement. Even small amounts of absorbed nitrogen make the titanium brittle. At 500° to 600° C., an oxide coating is formed, and at higher temperatures the gas diffuses into the lattice, causing brittleness. Titanium in ingot form has a density of 4.54, a specific heat of 0.142, a coefficient of linear expansion of 8.5×10^{-6} per degree Centigrade, and an electrical resistivity of 8 microhms per centimeter. Tests

after exposure for 450 hours at 1050° C. indicate that the room-temperature yield strength, ultimate tensile strength, per cent elongation, and hardness are not affected significantly. If rubbed against hard surfaces, titanium has the unusual property of producing marks or smears believed to be the result of chemical reaction.

Titanium occurs in two modifications: *alpha*, which crystallizes in the hexagonal system, is stable up to 900° C., and *beta*, having a body-centered cubic lattice, is stable above 900° C. The transition temperature was found to be influenced greatly by traces of oxygen and probably also by nitrogen. Its heat capacity varies uniformly from 6.507 calories per mole at 200° C. to 8.901 calories per mole at 817° C. and then increases to an extremely high value as the temperature approaches 900° C. Above this temperature the heat capacity seems to remain practically constant at 7.525 calories per mole, which value corresponds to that of the beta modification. Electrical resistance of the metal over the temperature range of 100° to 1000° C. was found to be sensitive to traces of oxygen whether free or combined, and over the same temperature range the thermoelectric force, as measured against gold, was also found to be variable and sensitive to oxygen.[51] Potter[52] found that the electrical resistance does not become a linear function of temperature at higher temperatures, as is approximately true for nontransitional elements. From resistance measurements, De Boer, Burgers, and Fast[53] determined the transition temperature to be 882 plus or minus 20° C.

Titanium and zirconium were reported to be isomorphous at nearly all temperatures in both the hexagonal and body-centered cube (high temperature) form.[54] By means of resistance measurements, the solid solution having an atomic ratio of 1 to 1 was found to have a transition point minimum at 545° C. Melting-point diagram of the system showed a minimum at 1575° C., with an atomic ratio of titanium to zirconium of 2 to 1. The transition point of pure titanium was found to be 885° C. From studies of X-ray diffraction patterns Hull[55] concluded that titanium crystallized in the holohedral class of the hexagonal system with an axial ratio of 1.59. The side of the unit triangular prism measured 2.97, and its height 4.72, Ångstrom units. Two sets of these triangular prisms make up the lattice, and the atoms of one set are in the center of the prisms of the other set. Precision measurements on a specimen 99.9 per cent pure demonstrated an hexagonal, close-packed structure with a_0 equal to 2.951, and an axial ratio c, equal to 1.590

Ångstrom units.[56] The density was computed as 4.49. According to Burgers and Jacobs,[57] the beta form of titanium, which is stable above 900° C., has a body-centered cubic lattice with two atoms in the unit cell. At temperatures just above this value, the length of the sides of the cube was found to be 3.32 Ångstrom units. Hull [58] also reported a centered-cube structure, with each atom surrounded by 8 other atoms. Hydrogen dissolved in the titanium changed the structure to a nearly cubic face centered lattice.[59] The paramagnetic susceptibilities of the system titanium-hydrogen differ from those of titanium.

Bridgman [60] subjected thin discs of titanium simultaneously to hydrostatic pressure up to 50,000 kg. per sq. cm. and shearing stress up to plastic flow. The curve of the maximum shearing stress plotted against pressure showed no break, indicating that titanium had no transition within the range studied. The electrical behavior further evidenced the absence of transition points.[61] Irregularities in the behavior of commercial titanium at temperatures above 500° C. were explained on the basis of impurities. The electrical resistance decreased slightly with increased pressure.[62] The pressure coefficient of electrical resistance at 30° C. gave an abnormal direction of curvature. Compressibility of the metal was observed to increase greatly with the temperature. Clausing and Moubis [63] observed that between 70° and 273° A. the change in electrical resistance with temperature was normal. At 0° C. the specific resistance and temperature coefficient were found to be 8×10^{-5} and 0.00469, respectively. Measurements were later extended to 2.2° A., and these showed that titanium gives normal temperature-resistance curves at the extremely low temperatures employed.[64] In magnetic fields up to 100,000 gausses, the increase of electrical resistance [65] was proportional to the square of the strength and, in stronger fields, followed a linear law. The electrical resistance of a single crystal of titanium containing 0.2 per cent zirconium and 0.03 per cent lead decreased greatly at 1.15° A., and the character of the curve obtained was interpreted as indicating true supraconductivity which could not be attributed to impurities.[66]

Mixter [67] burned pure ground titanium in powdered sodium peroxide and determined the heat of combustion to be 215,600 calories, but as a result of later work the value was revised to 218,500 calories. There was evidence of slow oxidation of the powder in air, even at room temperature. Specific heat curves for both titanium and titanium carbide, over the temperature range of 51° to 298° K., were normal.[68] From these data the entropies of titanium
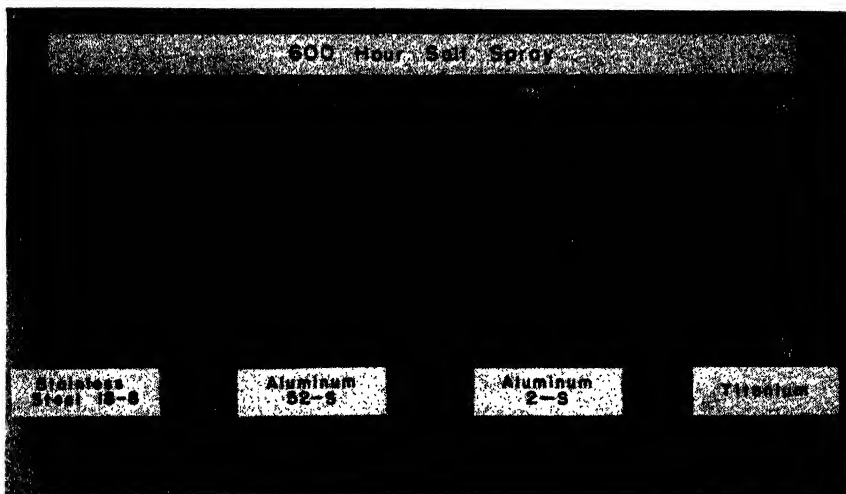
Figure 4. Samples of titanium, aluminum alloys, and stainless steel after exposure to salt spray for 600 hours
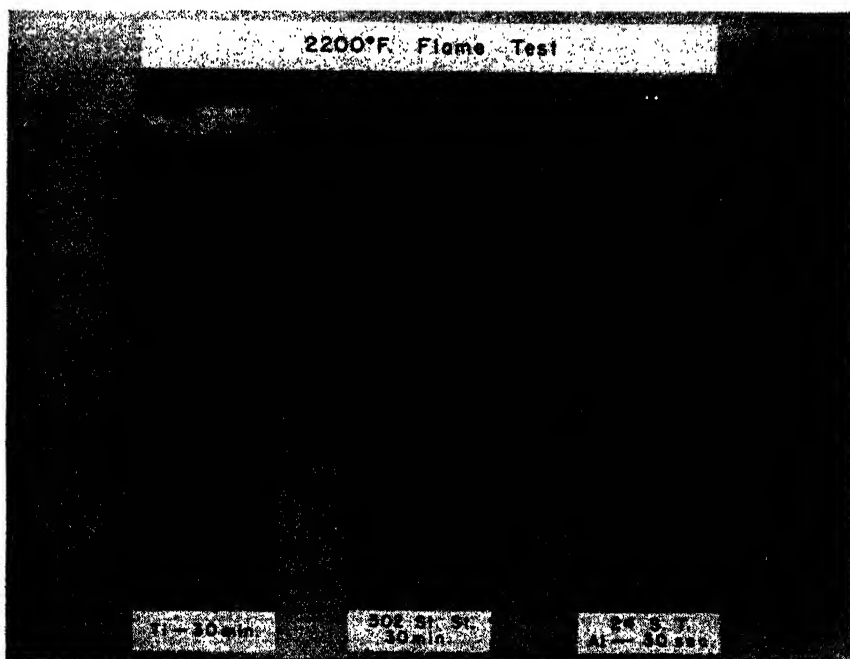
(Courtesy E. I. du Pont de Nemours and Company)

Figure 5. Comparative effect on titanium, stainless steel, and an aluminum alloy of exposure to a 2200° F. flame

(Courtesy E. I. du Pont de Nemours and Company)

and titanium carbide were calculated to be 7.24 and 5.8, respectively, at 98.1° C.

The coefficient of expansion was found to increase from 5×10^{-6} per degree at $-150°$ C. to 12×10^{-6} per degree at 650° C., indicating the absence of polymorphic transformation between the ranges of temperature studied.[69]

Kroll[70] investigated the effect of alloying elements on the deformability of titanium prepared by the reduction of the oxides, as determined by hot rolling. Oxygen showed the greatest tendency toward brittleness, and copper, sulfur, and all gases were harmful. The most ductile alloys were those containing nickel, iron, cobalt, molybdenum, tungsten, and tantalum. All additions increased the hardness. Titanium dissolved up to 10 per cent in molten lead and tin, and 12 per cent in molten zinc. With the first two elements it was mutually soluble in the molten state, but it was completely insoluble in the solid state.

Tests of explosibility[71] of dusts showed titanium to be one of the most explosive substances.

Molten titanium reacts with certain of the refractory oxides.[72] In vacuo, the molten metal reacts vigorously with aluminum oxide, actively with beryllium oxide, and slightly with thorium oxide. Of these highly refractory materials, only thorium oxide showed any promise as a crucible material for melting titanium.

POTENTIAL USES FOR TITANIUM METAL. Titanium has many actual and potential uses, based for the most part upon its properties as a silvery white, light, corrosion-resistant, tough, strong metal.[73] Among the metals available for construction there is a gap between aluminum and steel. Aluminum, with a desirably low density of 2.7, is easily formed and machined, but it has relatively low strength and is not resistant to corrosion. Iron, at the other extreme, can be alloyed to give high strength and resistance to corrosion, but its greater density, 7.87, is a decided disadvantage where weight is an important factor. Titanium, with a density of 4.5, coupled with its strength, ductility, high melting point, and noncorrosive characteristic, is the present outstanding candidate to fill this gap. It combines the properties of stainless steel with those of the strong aluminum alloys and possesses certain definite advantages over both. One outstanding advantage is its high proportional limit which is comparable to that of heat-treated steels and aluminum bronze, while its density is only a little over half that of these materials. As a result, wrought titanium is in a class by itself so far as the

weight of a section having a given proportional limit is concerned. Titanium would be a preferred structural material in aircraft design where a minimum weight combined with a continued high stress is important. Its resistance to corrosion would be an added advantage in airships for use over the sea or along the coast. A potential use of great importance is for making reciprocating mechanical parts in jet engines where heat and pressure are great. The metal seems almost ideal for ocean-going vessels because of its outstanding properties of lightness, strength, and great resistance to corrosion. As the cost of production is decreased, titanium will be used extensively for structural purposes. Even at the present high price it should find use in all sorts of diaphragms that are maintained under tension, particularly in microphones where weight is important. Titanium seems well suited for textile machinery where a considerable saving of power can be effected by using such a light, strong metal for high-speed spindles, spools, warp beams, and other moving parts. It does not stain the threads as do aluminum and magnesium alloys. Another of the important uses of the future is in suspension-bridge cables. These properties of titanium may prove important in the eventual utilization of atomic energy.

The surface-hardening property of titanium gives it a definite advantage over the really light metals in the construction of parts subject to frictional wear. It seems suited for automobile pistons, because, in addition to the characteristic properties of lightness and strength, it has a coefficient of expansion a little less than that of cast iron that is ordinarily used for cylinders. The high heat conductivity suggests its use for handles for aluminum pans and cooking utensils. It has been proposed for many sports uses, such as tennis rackets and fishing rods, where its excellent physical and working properties would be utilized. Combination of stainlessness, high proportional limit, and low modulus makes it an ideal material for springs, and its use should make possible the construction of greatly improved spring balances and watch springs. Its properties also recommend it for use in tool mountings where a certain amount of give is desirable to prevent breakage, and in making pen points and styluses. X-ray diffraction tubes with titanium targets are in the development stage. Rubbing titanium metal against a hard surface often produces a smear which is difficult to remove, and this characteristic is employed for a variety of purposes, including the production of very stable high electrical resistance glass, simply by marking the surface with a titanium point.[74] Such smears can be used to coat materials with a metallic film and to etch glass without the use

of hydrofluoric acid. Herenguel [75] investigated the use of titanium powder as a paint pigment.

The really large-scale use of titanium seems to depend only on its availability in suitable form at a price in line with the common metals such as iron and aluminum. It would be a notable exception to technological progress if titanium, with such desirable properties, failed to be an important engineering metal of the future. It is hoped that this book will encourage research on the production of low-cost titanium metal.

Electrolysis

Attempts by Keyes and Swann [76] to deposit titanium electrolytically from solutions of its simple salts in water or other solvents having high dielectric constants were unsuccessful, and they concluded that the metal could be plated only from highly ionized complex compounds. Porkony [77] succeeded, however, in electroplating it from a strongly alkaline solution of titanic oxide or hydroxide, employing a layer of the finely divided metal as cathode and copper or iron as the anode.

No cathode deposit was obtained on electrolyzing a weakly acid (0.1 normal) sulfate solution containing 1 mg. titanium dioxide per milliliter at a current density of 1 to 2 milliamperes per square centimeter.[78] Depending upon the acidity of the solution and the metal used for anode, titanium was precipitated as a basic sulfate, was reduced to the trivalent state, or was oxidized to pertitanic acid. With a cathode of gold or silver amalgam, pertitanic acid was formed, particularly if the two electrodes were separated by a porous kaolin partition and oxygen was passed into the cathode compartment. Employing a lead cathode, the yellow color of pertitanic acid changed gradually to the violet color of titanous ions, while the anode became covered with orange-brown peroxide. Basic titanic compounds were precipitated by employing a zinc cathode at lower acidities. A portion of the original solution, treated with a small proportion of hydrofluoric acid and neutralized with ammonium hydroxide, gave, on electrolysis with a lead cathode, a coating of black titanium monoxide. The addition of sodium sulfate prevented hydrolysis as the hydrogen ion concentration of the solution was reduced, and thin films of metallic titanium were deposited on cathodes of heavy overvoltage such as lead, tin, and zinc. A similar deposit was obtained from a more acid solution after addition of hydrogen peroxide. The metal was deposited from a 5 to 10 per

cent tartaric acid solution containing 0.5 to 1.0 per cent titanium dioxide at a current density of 30 milliamperes per square centimeter. According to Groves and Russell,[79] titanium was deposited on mercury at a rate of 0.2 g. per hour from a solution of the dichloride in 2 normal hydrochloric acid at a current density of 5 amperes per square centimeter. The metal was deposited on a copper cathode up to 1 micron in thickness from an electrolyte of sulfanilic acid and titanium hydroxide, using platinum or titanium-zinc anodes and a current density of 0.1 ampere per square decimeter at 20° C.[80]

The electrolysis of titanium tetrachloride [81] in the presence of commercial-grade hydrogen peroxide containing nitrogen and operating above 1000° C. gave a very thin yellow adherent coating of titanium nitride on the iron cathode. The nitride coating was quite resistant to weathering; for instance, the action of mineral acids and atmospheric agencies at 1000° C. was practically negligible. Electrodeposition of the metal was effected from solutions of complex organic salts of tetravalent titanium, having a concentration of titanium of 35 g. per liter or more, to produce a continuous adherent film. Such a coating, however, retarded corrosion of the iron base to a slight extent only.

The electrolytic reduction of tetravalent titanium to the trivalent state was found to proceed to completion on electrodes of lead, copper, and bright platinum, but was incomplete on dark platinum, since the equilibrium $Ti^{++++} + \frac{1}{2} H_2 \rightleftarrows Ti^{+++} + H^+$ was set up and could be established from either side.[82] From polarigraphic studies with the dropping mercury cathode, Zeltner [83] found that titanium gave an increase of current at 0.8 volt as a result of the reduction from the quadrivalent to bivalent state. No reduction was observed in alkaline solutions. The cathode curve [84] for polarization as a function of current density for tetravalent-trivalent electrolytes employing a mercury jet electrode showed two branches corresponding to the reaction $Ti^{++++} \rightarrow Ti^{+++}$ and $Ti^{+++} \rightarrow Ti^{++}$. The electrode potentials [85] of titanium in $\frac{1}{4}$ molar solutions of the tetrachloride and trisulfate were found to be 0.23 and 0.18 volt, respectively, as measured against the standard hydrogen electrode. With the latter electrolyte, the addition of a trace of hydrofluoric acid increased the potential to 0.22 volt. Hydrochloric and sulfuric acids caused a decrease in the potential, while alkalies gave the usual slight increase. Except with solutions containing hydrofluoric acid, replacement experiments did not agree with the electromotive force measurements.

The oxide layer formed by anodic polarization on titanium metal was found to be of the anatase crystal modification.[86]

Oxides

. Titanium forms four well-defined oxides: the monoxide, TiO, which is feebly basic; the sesquioxide, Ti_2O_3, which has decided basic properties; the dioxide or titanic acid, TiO_2, which is amphoteric; and the trioxide or pertitanic acid, TiO_3, which exhibits acidic properties only. The titanosic oxide, $TiO \cdot Ti_2O_3$, Ti_3O_4, or $Ti(TiO_2)_2$, does not seem to be definitely established, and others corresponding to the chemical formulas Ti_2O_5, Ti_3O_5, and Ti_7O_{12} have been reported, but evidence of their chemical individuality is not unequivocal. Hydroxides and hydrous oxides corresponding to most of these have been described.

DIOXIDE. From a practical standpoint, the dioxide is the most important member of the group. It is generally prepared by hydrolytic precipitation from titanic salt solutions (sulfate or chloride) by dilution, by heating, or by addition of an alkaline agent. Such products are in the hydrous form but the closely held water may be driven off by calcination at elevated temperatures.

The compound may also be obtained by the direct oxidation of titanium metal or the lower oxides, by heating the anhydrous tetrachloride with oxygen or air at high temperature, by decomposition of salts, and by electrolysis.

Bohm [87] noted that precipitated hydrous titanium oxide glowed brilliantly for a short time on heating to dull redness, and that the extent of the change and the temperature at which it took place depended upon the method of preparation of the sample. By Debye-Scherrer X-ray spectrograms, the glow was shown to be the transformation from the amorphous to crystalline state. Wohler [88] found, however, that the titanic acid precipitated from both hot and cold solutions showed this luminescence at 500° C., and he suggested that the phenomenon was due to a type of surface fusion or sintering. The effect appeared only with rapid rise of temperature.

After ignition at 1000° C., the compound became practically insoluble in hot sulfuric and hydrochloric acids; however, if the temperature of ignition does not exceed 700° C., solution in concentrated sulfuric acid is accomplished without great difficulty. Hydrofluoric acid is more effective, and fusion with potassium acid sulfate

or alkali metal bases converts the calcined product into a readily soluble form.[89]   It may be dissolved more conveniently in a hot mixture of sulfuric acid and an alkali metal or ammonium sulfate. A suspension of the solid compound in dilute sulfuric or hydrochloric acid assumed a pale lilac or light blue color on addition of metallic zinc, indicating the formation of titanous ion.[90]   Titanium dioxide may be volatilized [91] by heating with boron fluoride. It has been reported to react with liquid hydrogen chloride at low temperatures and with the gas at 200° C. to form a yellow basic dichloride, $Ti(OH)_2Cl_2$.[92]   In the presence of water it forms the trihydrate.

The oxide exists in three crystal modifications,[93] anatase, brookite, and rutile, all of which have been prepared synthetically. Experiments show that rutile, the most stable modification, is formed at the highest temperature, brookite at a considerably lower value, and anatase at a point still lower on the scale. The findings are also in agreement with the known occurrences of the three species in nature. Heating a single crystal of anatase between 800° and 1000° C. yielded an aggregate of rutile, but the transformation was too rapid to follow any certain direction.[94]   Brookite was converted into rutile in a comparatively ordered fashion by heating at 700° C., and in a partially ordered fashion by heating at 800° C. Pamfilov and Ivancheva [95] were not able to prepare titanium dioxide of the brookite structure from aqueous media. The product precipitated from solutions of its salts by thermal treatment in the laboratory had only rutile or anatase structure. Normally, sulfate solutions yield anatase directly, while halides and nitrates give rutile. Under special conditions, however, the results may be reversed. For instance, by seeding sulfate solutions with rutile nuclei all the titanium content may be precipitated in this form. Furthermore, solutions prepared by dissolving in sulfuric acid hydrous oxide precipitated from aqueous titanium tetrachloride have yielded rutile on hydrolysis. Titanium tetrachloride and other solutions, which normally yield precipitates of the rutile form, may be hydrolyzed in the presence of phosphoric or sulfuric acid so as to give anatase. Concentration and temperature of hydrolysis are also factors.

According to Bunting,[96] the stable form of titanium dioxide above 400° C. is rutile with a melting point of 1852° C. It formed no compound with silica, but an eutectic mixture containing 89.5 per cent silica by weight was obtained at 1540° C. With alumina, a compound corresponding to the chemical formula $TiO_2 \cdot Al_2O_3$ and

having a melting point of 1860°C. was produced, and at 1850° C. this compound formed an eutectic with alumina at 62 per cent aluminum oxide. Titanic oxide was readily crystallized from fused borax.[97]

Specific gravity varies from approximately 3.84 for anatase to 4.26 for rutile. It has the highest index of refraction of any white inorganic crystalline material, and ranges from 2.55 for anatase to 2.71 for rutile. The pure oxide has a yellowish tone, but finished samples of a pure white or even bluish cast may be produced, apparently as a result of converting a very small proportion of the material to the blue sesquioxide during the calcination process.

Baraleff [98] reported the molecular volume of titanium dioxide as 18.0. The heat of formation at constant volume,[99] as determined in a bomb calorimeter by using paraffin oil, was found to be 218.1 kg. cal., and the density at 21° C. was 3.863. At 20° C. and constant pressure, the heat of formation of the rutile modification was determined as 218.7 kg. cal.[100] The heat of formation of the oxide, under constant pressure at 19° C. derived from the heat of combustion, determined calorimetrically, was reported to be 225.3 kg. cal.[101] Entropy at 298.1°K. was found to be 12.45 e.u.[102]

Buttner and Engle [103] found that the dielectric constant of powdered titanium dioxide presented no anomaly within the temperature range of −180° to 0° C. The value decreased, however, with increasing temperature over the range of 20° to 300° C., by the same proportion for all wave lengths. From 20° to 120° C. this change was 8 per cent. At higher temperatures some reduction occurred, and slightly reduced samples showed a strong dispersion, with a minimum in temperature coefficient for wave lengths below 60 m. or above 350 m.[104]

From studies of three samples of rutile over a frequency range from 60 to 106 cycles and over a temperature range from 30° to 600° C., the dielectric constant [105] was found to be approximately 100. The value fell off slightly in the infra-red region, and it had a temperature coefficient of -8.2×10^{-4} per degree centigrade. The dielective losses were low, particularly at higher frequencies. In the higher temperature region an exponential relationship was observed between conductivity and the reciprocal of the absolute temperature.

The surface area [106] of finely divided titanium dioxide, as measured by the absorption of vapors of relatively volatile liquids, agreed well with values obtained from the absorption of nitrogen. Volumes of 13.8 square meters per gram were obtained for rutile.

Foek [107] measured the electric conductivity of compressed cylinders of oxides of titanium under various conditions. According to Earle,[108] titanium dioxide is an electrical semiconductor in which the current carriers are actually free electrons. Shomate [109] measured the heat capacities of rutile and anatase in the temperature range 52° to 298.16° K., and computed the molal entropies of rutile as 12.01 and of anatase as 11.93 at the highest temperature studied, 298.16° K.

A new system of triplets, B, has been found more recently in the band spectrum of titanium dioxide, in addition to the A, C, and D systems.[110]

Cathode rays acting on recently fused titanium dioxide excited three blue bands at 0.625, 0.550, and 0.425 micron, while the aged material exhibited only faint orange-red bands. Ultraviolet light had no effect, but under flame excitation a grayish-blue luminescence was visible at 425° C., which changed to red at 677° C., and finally to yellow at still higher temperatures. On heating to incandescence in an oxyhydrogen flame with hydrogen in excess, a reddish luminescence reached a maximum at 985° C., although with an excess of oxygen a modified blue glow was observed throughout all the visible region and at all temperatures below 1200° C.[111]

A composition of titanium in concentration of 10^{-5} to 10^{-1} with alumina, heated at 1300° C. for one hour, cooled quickly and excited in a Braum tube by cathode rays under 4000 volts, exhibited a faint violet luminescence.[112] Ions [113] of titanium were emitted on heating the oxide to a white heat on a tungsten filament.

SESQUIOXIDE. Lower oxides of titanium have usually been prepared by reduction of the dioxide. Reduction with hydrogen at 1200° to 1500° C. yielded primarily the sesquioxide, but at 1500° C. some monoxide was found in most tests.[114] A sample of the dioxide, heated in a stream of hydrogen for 20 minutes at 1000° C., lost only 4.64 per cent in weight as compared with a theoretical loss of 10 per cent for complete conversion to the sesquioxide.[115] According to Nasu,[116] within the temperature range of 750° to 1000° C., the equilibrium can be expressed as $2TiO_2 + H_2 \rightarrow Ti_2O_3 + H_2O$.

Amorphous hydrous titanic oxide was converted to the sesquioxide by heating at 800° to 1000° C.[117] with a carbonaceous reducing agent. Crystallization was promoted by the addition of 0.5 per cent zinc oxide or ammonium fluoride. A similar reduction was effected by calcining a finely ground mixture of the hydrous oxide with 2 to 20 per cent of a carbonaceous material such as sawdust,

sugar, or charcoal.[118] Solid solutions of titanium sesquioxide in the dioxide were prepared by heating the dioxide at 800° to 1100° C. in a nonoxidizing atmosphere with a reducing agent such as a titanous compound, aluminum, chromium, iron, or vanadium.[119]

According to Billy,[120] reduction by hydrogen, aluminum, and carbon failed to give well-defined lower oxides, but by reaction with an excess of the metal itself the sesquioxide was formed at 700° C. and the monoxide at 1500° C.

Titanium dioxide was found to be quite stable at its melting point, about 1800° C., but dissociated into the sesquioxide at 2230° C. The heat evolved in the reaction $1/2Ti_2O_3 + 1/2O \rightarrow TiO_2$ was determined as 99,000 calories. In the presence of carbon monoxide, carbon effected reduction to the sesquioxide at 870° C., but by employing a higher temperature or by melting it with carbon, a mixture of sesquioxide and carbide was formed. By heating the dioxide in nitrogen, incomplete conversion to the sesquioxide took place, and this was also true of reduction with hydrogen. This lower oxide melted at 1900° C. and tended to lower the melting point of titanium dioxide.[121] Ruff[122] obtained the sesquioxide, along with other lower oxides, by heating the dioxide in an electric vacuum furnace. The original material lost oxygen rapidly. It has also been prepared by the reaction of titanium tetrachloride and formaldehyde.[123]

Electrolysis,[124] under various conditions, of titanium dioxide dissolved in fused salts and mixtures (calcium chloride, calcium chloride and sodium chloride, cryolite, sodium pyrophosphate and sodium chloride), and of potassium titanofluoride (K_2TiF_6), dissolved in mixtures of fused sodium chloride and potassium chloride, gave in every case lower oxides of titanium instead of the metal.

The Debye X-ray method of following the reaction indicated that at 1000° to 1500° C. reduction of titanium dioxide by a mixture of hydrogen and nitrogen gave Ti_2O_3 and TiO.[125] Above 1700° C. some nitride was formed. At 1900° C. the dioxide was completely reduced in 3 hours, with carbon in nitrogen, to the carbide and nitride which formed a solid solution.

The specific heats of TiO, Ti_2O_3, Ti_3O_5, and TiN were measured between 52° and 298° K., and the molal entropies were computed as 8.31, 18.83, 30.92, and 7.20, respectively.[126] Naylor[127] measured the heat contents above 298.16° K. and developed the specific heat equations. TiO, Ti_2O_3, and Ti_3O_5 exhibited transition points.

According to Breger[128] the unit cube edges of the compounds titanium oxide, nitride, and carbide decrease with the atomic weight

of the nonmetal owing to decreasing radius, increasing ionization of titanium atoms, and increasing electron gas density.

The sesquioxide is a hard, violet-colored solid, crystallizing in the hexagonal system. It is readily oxidized to the dioxide, is slightly soluble in the latter compound, and imparts a bluish color. It is soluble in dilute sulfuric and hydrochloric acids, but is oxidized by nitric acid. From thermoelectrical data, the lattice energy [129] was calculated to be 3569.51 kilogram calories.

MONOXIDE. Titanium monoxide has been prepared by the reduction of the dioxide with various agents. Employing hydrogen, small yields were obtained at 1500° C.; reduction with charcoal at 1100° to 1500° C. gave a solution of the monoxide and titanium carbide,[130] varying from 33 to 60 per cent of the latter. Billy [131] obtained the compound by reducing the dioxide with magnesium metal. A mixture of titanium dioxide and titanium metal, pressed into pieces 4 by 40 millimeters in size and heated in an exhausted atmosphere at 1550° to 1750° C. for 2 hours, gave a sintered stick of golden yellow color. Chemical analysis corresponded to the composition of the monoxide, and X-ray examination confirmed the finding.[132]

The compound dissolved in dilute sulfuric acid with the evolution of hydrogen and it was insoluble in nitric acid, although oxidized to the dioxide. On heating the material in air, the finely powdered product became dark blue and crystalline after 1 hour at 400° C., gray-green after 1 hour at 600° C., and was converted rapidly to the dioxide above 800° C. Its density was 4.93, melting point was 1750° C., and specific resistance 2.49×10^3 ohms per centimeter. Hardness was about four times that of glass. It had a structure of sodium chloride type [133] with $a = 4.25$ Ångstrom units. The data indicated that it was not ionized. Reduction of titanium dioxide with calcium proceeded smoothly to the formation of the metal, but reduction with magnesium stops at TiO after the intermediate formation of Ti_3O_4.[134] Titanium monoxide of a deep chestnut color, on heating at 150° to 250° C. in the presence of oxygen, became deep violet as a result of the formation of Ti_2O_3; at 250° to 350° C. it changed to the deep-blue Ti_3O_5; above 350° C. it reverted to the dioxide. Reduction of TiO_2 with hydrogen gave Ti_3O_5 as the final product. Calcium and magnesium, molded into pellet form with titanium dioxide, produced TiO as the end product.[135] Reduction started at 500° to 575° C.

A product reported to be titanosic oxide, Ti_3O_4, was prepared by heating a mixture of the dioxide and microcosmic salt in a loosely

covered crucible in air. Cubic crystals of this composition were obtained by the high-temperature reduction of titanium dioxide. The chemical constitution was regarded to be $TiO \cdot Ti_2O_3$.

A blue oxide corresponding to the formula Ti_3O_5 was obtained by reducing the dioxide with hydrogen or carbon monoxide at 700° to 1100° C.[136] With the former gas, complete conversion was effected.

PEROXIDES. Acid solutions of titanic salts acquire a bright yellow color on addition of hydrogen peroxide, and the properties become quite different from those of the original compound. Since the coloration develops only on the addition of peroxides or per-compounds, the product is thought to have a peroxide structure. Sulfate solutions give an immediate precipitate with ammonium hydroxide, but from similar solutions containing hydrogen peroxide the precipitate is insignificant and becomes appreciable only after destruction of this agent. It follows that the introduction of active oxygen into the molecule of titanium oxide promotes formation of complex ions.[137] The coloration produced by adding hydrogen peroxide to solutions containing from 4 to 80 milligrams of titanium per liter proved stable over a period of 2 years.[138]

Titanium may be precipitated by hydrogen peroxide in alkali or ammoniacal solutions as peroxide hydrate, but it redissolves in an excess of the cold liquor. From such solutions, alcohol throws down a pertitanate, as, $K_4TiO_8 \cdot 6H_2O$. On adding hydrogen peroxide slowly to an ice-cold solution of titanium tetrachloride in ethyl acetate, an orange coloration first appeared, and later a white precipitate formed which contained titanium, chlorine, and hydrogen peroxide in the approximate ratio of 1 to 1 to 1. The product was very soluble in water, yielding a clear orange-colored solution. The apparent loss of three atoms of chlorine per molecule of tetrachloride can be attributed to oxidation to free chlorine by the hydrogen peroxide on partial decomposition of the ethyl acetate, with the formation of ethyl chloride and titanium acetate. Both solution and precipitate were thought to be hydrogen peroxide solvates of a monochlorotitanium compound.[139] Viscosity measurements indicated complex formation on adding hydrogen peroxide to aqueous titanium tetrachloride, and study of the movement of the ions in an electric field showed that the titanium was part of the anion.[140] Schwarz and Sexauer [141] prepared the peroxide of titanium in aqueous solution and extracted the uncombined water with ethyl alcohol at 0° C. Combined water and oxygen were then determined, and the ratio of titanium dioxide, oxygen, and water

was found to be 1 to 1 to 2. From these data they assigned the formula $TiO_2 \cdot O \cdot 2H_2O$.

On treating freshly prepared titanic acid with neutral hydrogen peroxide, or by treating a solution of titanium sulfate with this reagent and then adding ammonium hydroxide, a product was obtained which, after drying over concentrated sulfuric acid, yielded a yellow, horny mass of hydrated titanium peroxide or pertitanic acid, $TiO_3 \cdot H_2O$. The trioxide may also be obtained by dropping titanium tetrachloride into aqueous alcohol and adding a large excess of hydrogen peroxide. On adding ammonium hydroxide or carbonate, or potassium carbonate to the solution, a bright yellow precipitate corresponding to $TiO_3 \cdot 3H_2O$ formed after a time. At 0° C. the trioxide, in the presence of potassium and alcohol, yielded crystals of potassium peroxide hypertitanate, $K_2O_4 \cdot TiO_3 \cdot K_2O_2 \cdot 10H_2O$, and with sodium hydroxide a compound of the formula $(Na_2O_2)_4 \cdot Ti_2O_7 \cdot 10H_2O$ was obtained.

Work by Billy [142] indicated that the pertitanates are complex compounds with hydrogen peroxide and that they correspond to the chemical formula Ti_2O_5 rather than TiO_3, as generally assumed. Hydrates of pertitanic salts may be obtained by hydrolytic precipitation from dilute aqueous solutions. Analysis of the salt obtained at 10° to 20° C. corresponded to the chemical formula Ti_2O_5, but products thrown down at around 0° C. gave a ratio of titanium to oxygen of 2 to 5.27, which was far from the suggested formula TiO_3.[143] McKinney and Madson [144] suggested that titanium pentoxide may be a molecular compound of $TiO_2 \cdot TiO_3$, but they also pointed out the possibility of a ring structure such as

```
        O
        ‖
   Ti ——— O                    O = Ti — O
   |        |                          |
   |        O                          O
   |        |                          |
   Ti ——— O                    O = Ti — O
      \\
        O
```

By substituting peroxide groups for the oxygen atoms attached to the titanium atoms, a large number of different formulas can be postulated. Compounds of this type would exhibit isomerism and polymerism. In explaining the structure of such compounds, Hakomori [145] proposed induction valence which is produced by electrostatic induction and is not measurable by integral numbers.

Freshly prepared and well-washed titanium hydroxide dissolved in dilute aqueous hydrogen peroxide to give a clear yellow solution which exhibited colloidal properties. A suspension of 0.0035 mole titanium hydroxide in 50 ml. water treated with 0.4 ml. of 30 per cent hydrogen peroxide (also 0.0035 mole) cleared after one hour at room temperature and after a few minutes on warming. Larger proportions of hydrogen peroxide hastened dissolution, and smaller amounts gave solutions with pronounced opalescence. Addition of electrolytes effected almost complete precipitation, but higher concentrations of hydrogen peroxide reduced the recovery. Concentrated solutions solidified to gels on cooling.[146] However, titanic acid is quite soluble in hydrogen peroxide acidified with sulfuric acid and yields true solutions, as determined by the ultramicroscope.[147]

Ozone was evolved from peroxide sulfate compounds of titanium. The formula suggested for pertitanium sulfuric acid, a member of this group, is HSO_4-TiO_2-O-O-SO_3H.[148]

Potentiometric and calorimetric measurements indicated the formation of TiO_3 and $TiO_2 \cdot H_2O_2$.[149]

Colloidal Compounds

Titanic acid is generally considered to exist in two modifications, the alpha or ortho corresponding to the chemical formula $Ti(OH)_4$, and the beta or meta having the composition $TiO(OH)_2$. The former may be obtained as a voluminous white precipitate by adding aqueous ammonia or alkali metal hydroxides or carbonates to solutions of titanic chloride or sulfate, in the cold. It may also be prepared by decomposing potassium titanate with hydrochloric acid. The precipitate should be washed and dried in the cold, for if the temperature is raised, some meta variety is formed. As long as it remains fully hydrated, the ortho modification is soluble in dilute sulfuric and hydrochloric acids, and in the stronger organic acids, but loses water on heating and forms complex, less soluble products. It passes slowly into the meta form if allowed to remain in contact with water at room temperature, and more rapidly on heating. The ortho acid gives an orange-red coloration with tannin.

Metatitanic acid is precipitated directly from hot solutions of titanic salts by adding alkalies or by boiling; by the action of nitric acid on titanium metal, by drying the ortho acid in vacuum, or by heating it at 140° C. It is a white powder, insoluble in water, very

slightly soluble in dilute acids, and soluble in hot concentrated sulfuric acid.

From X-ray studies, Levi [150] concluded that both varieties were completely amorphous. The greater part of the water was found to be loosely bound by capillary or osmotic forces.[151] The preparations were represented as penetrated by canals of radii of the order of 100 Ångstrom units. The remainder of the water was considered as being bound in the interior of the titanic acid. Dehydration by the Van Bemmelen, the Bolte, and the thermal methods proceeded without interruption or breaks, showing that the hydroxides are not crystal hydrates of definite structure. The compounds were represented as holding water by adsorption (capillary forces). On heating to incandescence, the hydrous oxide became crystalline and was a mixture of anatase and brookite. At 1100° C., both changed to rutile.[152]

These differ primarily in the size and complexity of their ultimate particles as a result of the amphoteric nature of the compound. As a result of relatively greater surface, the orthotitanic acid precipitated from cold solutions has a greater absorptive capacity for dyes than metatitanic acid obtained from hot solutions. In general, the effectiveness of both varieties decreases with dehydration. Samples prepared from alkaline solutions absorbed basic but not acid dyes, while the opposite was true of products obtained from slightly acid solutions. Titanic acid precipitated from chloride solutions by calcium carbonate, however, absorbed both acid and basic dyes but had a low capacity. This difference in the behavior of samples obtained from acid and alkaline solutions may be attributed to the amphoteric nature of the oxide, resulting in the former case in the precipitation of a highly basic titanium salt, and in the latter of an alkaline titanate. Another possible explanation is that the positively and negatively charged colloidal particles are present as a result of hydrogen and hydroxyl ions absorbed from the medium. By the same reasoning, titanic acid obtained by precipitation with calcium carbonate is neutral and should have no acid or basic ions.[153]

No alpha acid prepared at 25° C. was detected, in the colloidal state, in hydrochloric acid solutions stronger than 0.25 normal, while with beta acid precipitated at 100° C. the colloidal condition persisted until the concentration of the hydrochloric acid reached 1.5 normal.[154] The mode of precipitation and the temperature of drying exerted considerable influence on the solubility.

From X-ray, phase rule, and potentiometric titration studies, Weiser and Milligan [155] concluded that the alleged ortho and meta

acids do not exist, and that the different preparations which can be obtained are not isomers but differ in size and extent of coalescence of the primary particles into secondary aggregates. Titania gel was found to be hydrous titanium dioxide. This work indicated that, in general, gelatinous precipitates of the oxides are not polymerized compounds or condensation products resulting from the splitting off of water from hypothetical metallic hydroxides, but, rather, that they consist of agglomerates of extremely minute crystals of oxides or simple hydroxides which hold large amounts of water by adsorption or capillary forces.

According to the same workers, hydrous titanic oxide gives X-ray diffraction patterns of the amorphous type and relatively sharp ring electron diffraction patterns.[156] This was interpreted as meaning that the oxide was crystalline, but that the primary crystal size was so small that the X-ray diffraction pattern consisted of broad bands. After aging at room temperature, gels of titanium dioxide gave weak X-ray patterns corresponding to anatase.[157]

Many compounds of titanium in solution have a tendency to assume the colloidal form[158] under a variety of conditions, and this has made studies of the general chemistry of the element more difficult. This property, objectionable to theoretical chemists, has been mastered by industrial research workers and is applied in the production of titanium pigments. Careful control of the formation of colloidal hydrous titanium dioxide and the conditions which exist during its subsequent coagulation are regarded as prime determining factors in the manufacture of titanium dioxide of highest pigmentary properties.

These compounds are unique in that they can exist in the colloidal state in solutions containing large proportions of electrolytes. For instance, dispersed systems, containing 60 g. colloidal titanium dioxide in a liter of a solution containing 400 g. sulfuric acid, may be prepared readily, and under most favorable conditions stable aqueous systems containing more than 600 g. colloidal titanic acid per liter can be obtained. Such solutions are almost as fluid as water and can be prepared commercially at a cost comparable to that of titanium dioxide pigment. Hydrolytically precipitated titanium dioxide serves as a convenient starting material. The washed pulp is treated with an alkali to neutralize the adsorbed sulfuric acid and washed until free of sulfates. Two grams concentrated hydrochloric acid is then added for each 100 g. of titanium dioxide, and on agitation the thick slurry becomes quite fluid. The peptization

process is readily reversible, and coagulation is effected by the addition of a small proportion of a sulfate or other polyvalent anion. Colloidal titanium dioxide dispersed in acid media acquires a positive charge, although in alkaline systems the charge may be reversed.

Colloidal solutions may be prepared in any degree of dispersion by peptizing titanic acid or hydrous oxide obtained by hydrolytic precipitation.[159] The washed pulp is first freed from sulfuric acid by treatment with ammonium or alkali metal hydroxide, followed by additional washing, and is then agitated with a small proportion of hydrochloric acid or chlorides of titanium or silicon to effect dispersion. Alternatively, both these stages may be carried out simultaneously by employing barium chloride which converts the sulfuric acid to an insoluble salt and liberates hydrochloric acid as a peptizing agent. In an example, 1 kg. of titanium oxide, or metatitanic acid precipitated by the hydrolysis of sulfate solution, was washed and treated with ammonium hydroxide to neutralize the residual sulfuric acid. The ammonium sulfate was then washed out and 20 g. concentrated hydrochloric acid was added. Peptization was immediately effected and the system became completely fluid. The product was dried and dehydrated for pigment use.

Stable solutions containing colloidal titanic oxide may be prepared by adding aqueous titanium sulfate to hot water and cooling the mixture before any appreciable precipitation has taken place.[160] Such dispersions may be coagulated by adding concentrated hydrochloric acid.

Colloidal titanium oxide in a coagulated, paste-like form was peptized by adding ammonium hydroxide or an organic base, such as methylamine, with agitation, until the product was slightly alkaline to litmus. On introduction of a large quantity of distilled water, a pseudo solution resulted, which appeared opaque in reflected light but transparent in thin layers.[161] Similar solutions were prepared by subjecting finely divided titanium dioxide, at moderate heat, alternately to the action of dilute acid and dilute alkaline solutions. After each treatment the product was washed with distilled water, and the process was continued until transformation to the colloidal state was complete.[162]

By reducing a 1 per cent solution of palladium chloride, together with 15 per cent aqueous titanium tetrachloride which had previously been almost neutralized with sodium acetate, and heating the system to boiling, a solution consisting of colloidal titanium dioxide with adsorbed palladium was obtained.[163] Muller [164] found that

colloidal solutions of titanium oxide could be produced and stabilized by an aqueous suspension of cherry gum. Mixtures were separated by this procedure.

From a study of the peptization of titanium hydroxide and of the resulting solution, Parravano and Caglioti [165] found that the particles were charged positively, but that the sign of the charge could be changed by alkaline reagents such as sodium hydroxide, ammonium hydroxide, and sodium phosphate, or by precipitation of the colloid by the tartaric acid method. Among organic compounds, fuchsin showed an extremely high flocculating power. Electrolytes were not only adsorbed at the surface of the titanic oxide micelle, but were probably held within the particles in the frozen state, and, consequently, sometimes hindered the polymorphic transformations during calcination of the flocculated products. Gels prepared by hydrolysis were extremely lyophilic. Hydrochloric acid and titanium tetrachloride were employed as peptizing agents.

Colloidal titanium dioxide was found to behave as a typical positively charged hydrosol.[166] Ethyl and methyl alcohols sensitized this sol toward a majority of coagulating agents. Dispersed titanic oxide precipitated from aqueous tetrachloride migrated to the anode under a potential difference,[167] and such particles were deposited electrophoretically from a suspension in an aqueous solution of a soap or an alkali salt containing an amphoteric metal in the acid radical, such as potassium zincate or sodium hexametaphosphate.[168] The deposited particles were enclosed in a film of fatty acid or metallic oxide so that their original form was maintained and they were not plastic in the dry condition.

Studies of dialysis coefficients indicated that titanic acid is capable of forming molecularly dispersed acids, and that these are unstable and that they alter rapidly to colloidally dispersed hydrous oxide.[169] Dispersions of saponified titanic acid esters stiffened to the consistency of jelly after standing for 6 to 22 hours. According to Joseph and Mahta,[170] chlorides of potassium, magnesium, and aluminum, dissolved in a mixture of water and methyl, ethyl, or propyl alcohol, increased the viscosity and rate of coagulation of dialized titanium dioxide solution beyond that observed with aqueous electrolytes. The periodic nature of the time-viscosity curves disappeared with increased purification of the colloidal material. The autocatalytic nature of the coagulation process disappeared on progressive dialysis.

Colloidal titanium oxide obtained by heating dilute tetrachloride solutions in contact with air acted as a strong protective colloid.[171]

Titanium hydroxide sols, prepared by dropping the tetrachloride into water at 18° C., could not be completely freed of hydrochloric acid by dialysis. Such a solution, containing 15.2 g. titanic oxide per liter, became gradually more viscous on prolonged dialysis and coagulated to a gelatinous mass at a hydrogen ion concentration corresponding to pH of 4.1. The particles adsorbed appreciable amounts of anions from solutions of sodium and potassium salts. Adsorption of hydroxyl ions was relatively small, and their high coagulating power was due to the removal of hydrogen ions by neutralization. The sols adsorbed more anions than cations, resulting in liberation of hydroxyl ions. Titanic hydroxide acted more basic than acidic, and the stability of the sol precipitated at 18° C. was attributed to the adsorption of tetravalent titanium ions.[172]

Hydrosol of titanium dioxide, prepared by peptization of suspensions of the hydrolysis product of tetrachloride solutions, was treated with various compounds by Thomas and Stewart.[173] Addition of potassium salts resulted in an increase in the pH, the degree of which decreased in the following order of anions: citrate, maleate, oxalate, succinate, propionate, tartrate, lactate, sulfate, and nitrate. The decrease in hydrogen ion concentration was ascribed to the substitution of anions for hydroxyl groups of the hydrosol. Aging at room temperature resulted in a slight increase in acidity, and boiling accelerated this effect as a result of the formation of oxo complexes of the type shown below.

$$(H_2O)_4 - Ti \underset{O}{\overset{O}{\diamond}} Ti - (H_2O)_4$$
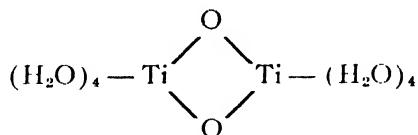
Potassium salts of citric, lactic, and tartaric acids, potassium hydroxide, and ammonium hydroxide formed anionic micelles because these ions displaced sufficient water groups to form negatively charged particles. Oxalic, tartaric, malic, and sulfuric acids peptized hydrous titanic oxide to anionic micelles, while nitric, hydrochloric, acetic, formic, and propionic acids yielded positively charged particles. Succinic acid had no peptizing effect. These data indicate that the ability of the acid to disperse titanium dioxide depends upon the strength of the acid and the capability of the anion to displace the water groups.

Vasilev and Deshalit [174] coagulated titanium dioxide sols with sodium sulfate and then titrated the products potentiometrically with

barium and calcium chlorides. On precipitation of the sulfate ions the material became peptized and at the same time chloride ions were again adsorbed. By this method the same sample could be alternately peptized and coagulated many times. Measurements carried out on such solutions showed that the activity value of the hydrogen ions increased almost linearly with increasing sol concentrations.[175]

Negative titanium dioxide sols showed exchange adsorption of cations and replacement of hydrogen ions. On the other hand, positive sols did not dissociate on dilution to yield hydrogen ions and corresponding anions, and the charge on the colloidal particles remained unchanged.[176] Gold sols assumed a purplish color on addition of titanium compounds.[177]

GELS. Patrick[178] prepared titanium dioxide gels by drying the hydrogel obtained from colloidal titanic acid solutions in a current of air at 75° to 120° C., and then raising the temperature slowly to 300° to 400° C. By washing the hydrogel with water at 21° to 80° C. before drying, a gel was obtained whose apparent density was less affected by strong heating.[179] Hard, tough gels having a density below 0.5, after being subjected to a temperature of 871° C., were prepared by heating the hydrogel slowly to 79° to 163° C. under conditions which did not permit dehydration, followed by slow cooling.[180] This heat treatment was carried out by passing heated gas saturated with water vapor over the hydrogel immersed in water, by circulating heated air repeatedly over the material in perforated trays in a drying chamber, or by soaking the washed hydrogel in strong sulfuric acid which reacted with the water to produce the desired temperature rise, 50° to 135° C. The hydrogel could be washed before or after the treatment, or the dried gel could be washed. A similar product, prepared by heating a dilute sulfate solution of titanium with 20 per cent aqueous ammonia, was washed by decantation, coagulated with acetic acid, again washed to remove soluble salts, and dried at 100° to 110° C. The porosity of titania and alumina gels was found to be approximately equal, and the higher activity of the latter was ascribed to smaller pores.[181]

Stowener[182] neutralized an aqueous solution of titanium tetrachloride at a temperature below atmospheric to obtain a precipitate which was washed and dried to yield a hard, absorbent gel. A product of improved properties was obtained from hydrogels which had been previously purified by treatment with strong sulfuric, nitric, or hydrochloric acids.[183] Similarly, Barclay[184] mixed equal quantities of 10 per cent solutions of titanium sulfate and aluminum sulfate at —2° C. and added slowly, with stirring, dilute aqueous

ammonia until the alkalinity of the system was 0.005 normal. The precipitate was washed and dried to yield a hard, stable, and highly porous composite gel.

Vibrant jellies [185] were obtained on neutralizing a solution of sodium titanate in 33 per cent hydrochloric acid by the dropwise addition of aqueous alkali carbonate (sodium carbonate).

Only those inorganic gels which contain hydrogen, replaceable by silver, are considered to be true hydroxides, and since the corresponding compounds of titanium do not react to form silver salts, Krause [186] classified them as hydrated oxides. Passerini [187] found that the water in titania gel gave the same infrared absorption bands as pure water, and concluded that the water was absorbed physically by a phenomenon similar to capillarity. Dehydration curves of hydroxy gels of H_2TiO_3 and $H_2Ti_2O_5$ passed through phases of changing composition and through singular points corresponding to "daltonites." [188] Auger [189] observed that titanium dioxide gel was only slightly soluble in basic solutions, and that it varied from 20 mg. per liter in 10 per cent sodium hydroxide to 1200 mg. per liter in 40 per cent potassium hydroxide. It was insoluble in a saturated sodium carbonate solution. Bicarbonates seemed to form a double carbonate which hydrolyzed very readily.

The sorptive power of titania gel for sulfur dioxide, as measured by contact for 5 hours at 0° C. under a pressure of 1 atmosphere, varied according to the method of dehydration and activation.[190] Concentration of titanium dioxide, the precipitant added, and the method of coagulation were of minor importance. Sulfate ions were more effective than chloride, and the presence of a small proportion of ferric oxide increased the activity to a moderate degree. Low temperature of dehydration decreased the sorptive power. The water content was the most important factor, and gels, regardless of dehydrating conditions, had a maximum sorptive power corresponding to an optimum proportion of water. At 16° C., under a pressure of 1 atmosphere, the gel adsorbed 8.5 per cent of its weight of ammonia. It was found to be an excellent adsorbent of many organic compounds, and, at room temperature and 1 atmosphere pressure, absorbed 32 per cent of its weight of benzene, 30.4 per cent of acetone, 55.4 per cent of chloroform, 43.2 per cent of carbon disulfide, and 27.3 per cent of ether.[191]

Higuchi [192] studied the sorption and desorption of sulfur dioxide within the temperature range of −40° and 40° C. and explained the hysteresis phenomena on the basis of the capillary adsorption theory. Sorption and desorption of gases and

vapors by titania gel at higher pressures exhibited hysteresis, but a low-pressure, reversible equilibrium occurred.[193] Similar studies,[194] at temperatures from —22.5° to 50° C., revealed that Polanyi's adsorption equation was more applicable over the entire range than Patrick's formula which held at lower temperatures. The process proved to be not strictly reversible. Sorption and desorption isotherms of methyl alcohol, ethyl alcohol, normal and iso-propyl alcohols, monochlorobenzene, toluene, hexane, heptane, acetone, and ethyl acetate by titanium dioxide gel were measured at 0°, 10°, 20°, and 30° C., and as in the previous work, the isotherms showed a hysteresis loop in the range of high relative pressures.[195] This characteristic indicated two phenomena, namely, adsorption of the vapors on the surface of the gel and capillary condensation of the sorptives in pores of the gel. Acetone acted somewhat anomalously. The permanence of the hysteresis loop [196] in the water vapor-titania system through 30 adsorption-desorption experiments was established by measurements on a McBain-Bakr balance at 30° C. The results supported the cavity concept for permanent hysteresis effect with rigid gels.

Titania gels break down on standing, to give granular precipitates.[197] An approximate value of 22,000 calories for the energy of activation was determined, as compared with 17,000 calories for silicic acid gel. Acidic mixtures set more rapidly with increases in the pH, the titania content, or the temperature. Gels set at a higher temperature were liquefied by rapid cooling.

Further work by Klosky [198] indicated that titania gel was a poorer adsorbent and catalyst support than silica gel.

A coprecipitated titania-silica gel [199] was prepared by passing a stream of nitrogen through titanium tetrachloride at 99° C., and then into a violently agitated dilute solution of sodium silicate, at such a rate of flow that all the titanium tetrachloride was absorbed before reaching the surface of the solution. The mixed precipitate was separated, washed, and dried.

Chapter 7

THE CHEMISTRY OF TITANIUM SALTS

Sulfates

Titanium forms di-, sesqui-, and mono-sulfates, as well as a number of basic, double, and complex compounds, and hydrates.

DISULFATE. The disulfate, $Ti(SO_4)_2$, can be obtained by the action of hot sulfuric acid on the dioxide and may be crystallized from fuming sulfuric acid, but it decomposes on contact with even traces of moisture. Preparation by oxidation of the sesquisalt with nitric acid has been reported. Von Bichowsky [1] added concentrated sulfuric acid to hydrous titanic oxide slowly to avoid local overheating, and heated the mixture carefully just below the boiling point until sulfation was complete. The product was reported to be the disulfate.

Tetravalent compounds are known, containing a much lower proportion of sulfuric acid than that corresponding to the normal salt. For example, sodium hydroxide or other alkalies may be added to solutions of normal sulfates in such proportions as to reduce the ratio of sulfuric acid to titanium dioxide to 1 to 1 by weight, or even less, without causing a precipitate. Such acid-poor solutions may also be produced directly from the ore or the precipitated oxide. Titanium oxytrisulfate, $TiO_2(SO_4)_3 \cdot 3H_2O$, has been obtained by heating a solution of the dioxide in sulfuric acid in a closed tube at 120° C. On raising the temperature to 225° C., however, it converted to anhydrous titanyl sulfate. There is experimental evidence to indicate that the titanyl salt is the only sulfate of tetravalent titanium stable enough to persist under ordinary conditions, and it is this compound which forms on reacting ilmenite ore with sulfuric acid in the first stage of the commercial process for pigment manufacture. Such solutions give the dihydrate ($TiOSO_4 \cdot 2H_2O$) on crystallization, and they are readily hydrolyzed by heating or dilution to yield oxide of the same type as the more acid solutions corresponding to the normal salt.

A number of hydrates have been reported. The pentahydrate was obtained by boiling titanic acid with alcoholic sulfuric acid, followed by evaporation of the solution.

Crystalline titanyl sulfate having two molecules of water has been obtained from the product formed by heating hydrous titanic oxide with 2.5 parts concentrated sulfuric acid or with an excess of dilute acid at 60° to 120° C.[2] The crystals were washed with dilute sulfuric acid, in which they are only slightly soluble, although solutions containing up to 400 g. titanium dioxide equivalent per liter were prepared by dissolving the salt in water. The crystalline dihydrate was also prepared by heating a solution containing 1 to 15 per cent titanium oxide and 35 to 40 per cent free and combined sulfuric acid.[3] The crystals were washed with alcohol to remove adhering liquor. Kirkham and Spence[4] obtained a fine granular form of titanyl sulfate by heating a solution of specific gravity 1.50 to 1.75, containing 4 to 12 moles of sulfur trioxide to each mole of titanium dioxide at 90° to 135° C., with constant agitation. The dihydrate was prepared in 94 to 98 per cent yields by dissolving commercial titanium dioxide in hot 50 to 60 per cent sulfuric acid at the ratio of 4.5 to 3.5, and further heating the syrupy mass at 95° to 100° C. for 3 to 4 hours, with stirring, until precipitation was completed.[5] The crystals were filtered, washed with acetone or alcohol, and dried at 70° to 80° C.

Water-soluble titanic and titanyl sulfates in solid form were produced by spraying saturated solutions in a finely divided state into a current of air at a temperature of 250° to 350° C.[6]

Solutions of low content of free sulfuric acid for use in tanning and mordanting were obtained from regular titanyl or titanic sulfate liquors such as are prepared from ilmenite by adding ortho or meta titanic acid at not over 60° C. to react with the free acid.[7] Concentration of the neutralized solution was effected by evaporation under reduced pressure.

The titanium content may be separated from a sulfate solution containing iron and other impurities by adding a sulfate of an alkali metal or ammonium which forms a relatively insoluble double sulfate with the titanium.[8] Such compounds are quite stable to heat and may be prepared at elevated temperatures to obtain higher concentrations, and consequently higher yields, by crystallization on cooling. In an example, the solution obtained by dissolving 1000 parts of a reaction product of ilmenite and concentrated sulfuric acid containing 17 per cent titanium dioxide in 2500 parts of water was heated quickly with 400 parts of potassium sulfate at 95° C. The solution was filtered and cooled to 0° to 5° C., at which temperature the double sulfate crystallized with a yield of 65 to 75 per cent of the titanium. Most of the remainder was recovered by evapora-

tion or hydrolysis. Wohler and Flick [9] separated sulfates of titanium and iron, as obtained from ilmenite, by selective dissociation with heat. Ferric sulfate decomposed at 715° C. and titanic sulfate at 635° C. so that if the mixed compounds were heated at a temperature between these limits in a stream of sulfur trioxide, the latter was converted to the insoluble oxide without altering the former.

A basic titanium sulfate, insoluble in water but soluble in acids and containing 0.25 to 0.50 mole sulfur trioxide per mole of titanium dioxide, was precipitated from a titanic sulfate solution under controlled but incomplete neutralization with calcium carbonate at temperatures below 50° C. [10] Any iron present was held in the ferrous state. McCoy [11] converted basic titanium sulfate into a water-soluble form by treating it with fuming sulfuric acid.

From a study of the system, titanic oxide, sulfur trioxide, and water at 150° C., Sagawa [12] found that the solid phase consisted of these components in the ratio of 6:5:4, 1:1:1, 1:1:0, and 2:5:5. Reinders and Kies [13] investigated the solubility of hydrous titanium dioxide and of hydrous titanium sulfate in sulfuric acid-water mixtures at 25° C. A triple point was observed at 38.1 per cent sulfuric acid and 3.5 per cent titanium dioxide. The solubility of the sulfate in water or dilute acid was high, decreased to 0.05 per cent in 65 per cent sulfuric acid, and again increased in more concentrated acid. These solutions, particularly in water and dilute acid, were metastable but actually remained clear for months.

A number of double sulfates are known. Typical of the group are titanic potassium sulfate, titanic sodium sulfate, and titanic calcium sulfate.

According to Miyamoto, [14] hydrogen reacts with titanic sulfate $Ti(SO_4)_2 \cdot 3H_2O$, in a silent electric discharge to yield hydrogen sulfide. In dilute solutions the compound gave a color reaction with ascorbic acid. [15] At pH of 3.0, a yellow coloration developed which gradually changed to an intense reddish brown at pH of 4.6 and disappeared at pH of 5.2. In alkaline solutions the color was pale rose.

SESQUISULFATE. Titanous sulfate $Ti_2(SO_4)_3$ may be prepared readily by the electrolytic reduction of the tetravalent salt in aqueous solution, and if the introduction of impurities is not objectionable, metallic zinc or iron, sodium thiosulfate, or other reducing agents may be employed. To a crude titanic sulfate solution obtained from ilmenite, McKinney [16] added a stabilizing agent (citric, tartaric, or oxalic acid, or their soluble salts) and treated the product

with calcium hydroxide to remove excess sulfuric acid, followed by hydrogen sulfide to precipitate the iron. The filtered liquor was then electrolyzed to reduce the titanium to the trivalent state. The stabilizing agent prevented hydrolysis during the initial purification steps. Such a solution is used in the discharge of coloring agents employed in dying textiles. Spence and Craig [17] found that more stable solutions can be obtained by reducing aqueous titanic sulfate or chloride with aluminum than by dissolving the lower oxide directly in acid. Iron-free titanous sulfates, pure enough for use in refined analysis, were prepared by the electrolytic reduction of potassium titanium oxalate, [18] $K_2TiO(C_2O_4)_2 \cdot 2H_2O$.

Titanous sulfate is a bluish, crystalline solid, soluble in water. The compound does not hydrolyze in solution under normal conditions, but it is slowly oxidized by air to the tetravalent state, and at a more rapid rate in the presence of a small amount of an added copper compound which acts as a catalyst. [19] It is a strong reducing agent and precipitates metallic copper from moderately concentrated solutions of cupric salts. [20]

The sesquisulfate forms double salts with sodium, potassium, and ammonium sulfates, which may be crystallized from solution as hydrates, $3Ti_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 18H_2O$ and $Ti_2(SO_4)_3 \cdot Na_2SO_4 \cdot 5H_2O$. It forms alums with rubidium and cesium; cesium titanium alum, $Cs_2SO_4 \cdot Ti_2(SO_4)_3 \cdot 24H_2O$, was made by Piccini [21] in 1895. Hydrous titanic oxide was dissolved in dilute sulfuric acid, the proper proportion of cesium sulfate was added, and the solution was electrolyzed to reduce the titanium to the trivalent state. A deep violet color was developed and crystals of alum separated from the solution. Rubidium titanium alum, [22] $Rb_2SO_4 \cdot Ti_2(SO_4)_3 \cdot 24H_2O$, was prepared by the same method.

MONOSULFATE. Titanium monosulfate, corresponding to the chemical formula $TiSO_4$, has been prepared by dissolving metallic titanium in dilute sulfuric acid, and the salt has been obtained in crystalline form by evaporating the solution. It has also been prepared by dissolving the monoxide in dilute sulfuric acid.

Ehrlich [23] found that oxygen dissolved in metallic titanium up to the ratio of 1Ti to 0.45 O. The lattice constants and the mole volume changed only slightly.

Chlorides

Titanium forms well-defined di-, tri-, and tetra-chlorides, as well as a number of basic and complex salts and hydrates.

TETRACHLORIDE. According to Vigoroux and Arrivant,[24] titanium tetrachloride was first prepared by George in 1825 and later by Dumas, Wohler, Merz, Demarcay, and Moissan. The more common methods comprise the direct action of chlorine gas on a great variety of titaniferous materials, including the relatively pure metal, alloys, carbide, cyanonitride, the dioxide, and ores, at elevated temperature. However, employing oxygen containing raw materials such as ilmenite, rutile, or the processed oxide, a carbonaceous reducing agent is added to the charge to combine with the oxygen. Mixtures of chlorine and gaseous hydrocarbons (coal gas) have also been employed in the absence of solid carbon.

The compound has also been obtained by the reaction between titanic oxide and carbon tetrachloride in a sealed tube at elevated temperature, and by the action of carbon tetrachloride, chloroform, and sulfur chloride on heated titanic oxide.

As a rule the metal and its alloys dissolve in hydrochloric acid, but because of the reducing conditions, lower chlorides are formed largely.

Titanic chloride obtained by the chlorination of titaniferous materials usually has a yellowish to reddish color which has been attributed to vanadium oxychloride, ferric chloride, and dissolved chlorine. Such products may be purified by redistillation after treatment with sodium amalgam [25] or metallic gold, silver, mercury, iron, carbon, copper, bronze, bismuth, tin, cadmium,[26] iron, antimony, zinc,[27] lower valent titanium compounds [28] which may be formed in place by reducing a portion of the tetrachloride, as with hydrogen, polymerizable organic compounds such as rubber and drying oils,[29] crystalline ferrous sulfate,[30] an active sulfide,[31] or a heavy metal soap.[32] The crude tetrachloride may also be purified by bringing the vapor in contact with an absorbent such as silica gel, activated alumina, or bentonite.[33]

Titanium tetrachloride dissolves in water to form clear solutions which are hydrolyzed readily to yield a series of basic chlorides, $TiCl_3(OH)$, $TiCl_2(OH)_2$, $TiCl(OH)_3$, and finally $Ti(OH)_4$ or hydrous titanic oxide. Similar solutions may be obtained from another approach by dissolving orthotitanic acid in hydrochloric acid, or by adding an alkaline earth chloride (barium chloride, calcium chloride) to sulfuric acid solutions of titanium. The insoluble alkaline earth sulfate formed may be removed by filtration or settling. Stannic chloride was found to exert a considerable protective action [34] against flocculation of titanium tetrachloride solutions.

Anhydrous titanium tetrachloride is a colorless liquid which fumes strongly in moist air. Thorpe,[35] in 1880, determined the

specific gravity at 0° C. to be 1.7604, and the boiling point as 136.41° C. Specific gravity decreased to 1.74 at 10.1° C., and to 1.52 at the boiling point. Later, Sagawa [36] found the specific gravity at 0° C., and the molecular weight to be 1.76139 and 107.83, respectively, and the viscosity coefficient 0.007921 at 20° C. and 0.007458 at 25° C. The fluidity [37] from −15° to 50° C. was found to be a linear function of the specific volume. The solidification temperature has been reported by various workers from −23° to −30° C. From freezing point data of dilute solutions, Nasu [38] calculated the heat of fusion as 12.90 calories per gram. Arii [39] measured the vapor tension from 25° C. to boiling and determined from the pressure temperature curves that the boiling point should be 136° C., while the experimental equation gave 135.8° C. The molecular heat of vaporization, as calculated by the Claussius-Clapyron equation, was 8960 calories at 25° C. and 8620 calories at the boiling point. The Trouton constant was found to be 21.07, showing that the tetrachloride is a normal liquid. Specific heat of the liquid between 13° and 99° C. was found to be 0.19, and that of the vapor from 163° to 271° C. was 0.13. Heat of solution was determined as 58.5 calories. Spencer [40] determined the empirical heat capacity equation of gaseous titanium tetrachloride.

According to Bhagavantam, [41] molecules of titanium tetrachloride show a lack of optical symmetry. Diffraction patterns [42] obtained, on allowing an electron beam to penetrate vapors of the tetrachloride at right angles, were characteristic of a single molecule of the gas or vapor. The atomic distance was found to be 3.61 Ångstrom units, and the atomic form tetrahedral. Lister and Sutton [43] investigated the structure of $TiCl_4$ and $TiBr_4$ by electron diffraction of the vapors. Where the configuration would have an important effect upon the mode of scattering, it was found that the assumption of a tetrahedral molecule was entirely satisfactory. The bond lengths in Ångstrom units were Ti-Br 2.31 and Ti-Cl 2.18. Index of refraction measurements also showed the tetrachloride molecule to be a regular tetrahedron, with no dipole moment, and an electron polarization of 43.24 in carbon tetrachloride. [44] The atomic radius of titanium was determined as 1.51 Ångstrom units. The compound was found to be diamagnetic, with a specific susceptibility at 35° C. of $−0.287 \times 10^{-6}$. The paramagnetism of other compounds of titanium was explained as being due to the unsymmetrical nature of the valency links, and that of titanium as being due to two pairs of valency electrons being in different orbits. [45] According to Siertsema, [46] titanium tetrachloride

is the only diamagnetic substance which shows negative magnetic rotation. Its parachor was reported to be 262.5, and the atomic parachor for titanium 45.3. Viscosity [47] varied from 34.03 at 13° C. to 26.65 at 75° C. Delwaulle and François [48] observed that the fourth line of the Roman spectra of titanium tetrachloride is a doublet, and that the chlorobromides exhibit three new frequencies.

Titanium tetrachloride does not conduct electricity. It is miscible with organic solvents, and the molecular conductivity [49] of the compound in methyl and ethyl alcohols resembles that of true salts and increases with dilution. It also shows a high conductivity in acetonitrile.[50] Urbain and Schol [51] found that a potential sufficient to cause an arc to burst out in the midst of titanium tetrachloride dielectric caused an intense liberation of chlorine.

The approximate free energy of the reaction with water was calculated as −16.6 calories.[52] Roth and Becker [53] determined the heat of formation of titanium dioxide (rutile), at constant pressure at 20° C., to be 218.7 ± 0.3 kilogram calories, and from this value calculated the heat of formation of the tetrachloride to be 185 kilogram calories. Entropy calculations [54] from spectrographic data and from the third law of thermodynamics gave values of 84.4 and 81.5, respectively.

The thermal diagram of the system titanium tetrachloride-hydrochloric acid showed the existence of the compounds $TiCl_4 \cdot 6HCl$ and $TiCl_4 \cdot 2HCl$, melting congruently at −86° and −30.8° C., respectively.[55] Titanium, antimony, tin, arsenic, and phosphorus formed halides with readily interchangeable halogen atoms so that, on bringing them together, reciprocal conversion took place and the original compound could not be isolated in the solid or gaseous form.[56]

A solution of titanium tetrachloride in ethyl alcohol formed with anhydrous hydrogen peroxide an insoluble white addition product which was considered a coordination compound of the tetrachloride and hydrogen peroxide.[57] It slowly assumed a red color on standing. Decomposition was accompanied by the liberation of oxygen, hydrogen peroxide, and water.

A series of chlorosulfonate chlorides of titanium has been reported.[58] The monochlorosulfonate trichloride was obtained by the action of chlorosulfonic acid on titanium tetrachloride, and the dichlorosulfonate dichloride in low yields was formed by the action of sulfur trioxide in great excess. All were yellow crystalline compounds unstable in the presence of water. In 1879 Clausnizer [59] prepared a yellow amorphous solid, corresponding to the chemical

formula $ClSO_2 \cdot O \cdot TiCl_3$, by adding sulfur monochloride to titanium chloride. Thermal analysis showed that titanium tetrachloride and SO_2Cl_2 reacted to form $TiCl_4 \cdot 2SO_2Cl_2$.[60] Titanium tetrachloride reacted with phosphorus trichloride to give small nearly octahedral grains of $TiPCl_7$, and with phosphorus tribromide to form red acicular crystals of TiP_2Br_{10}.[61] Gnezda [62] prepared a number of complex compounds, some of which formed colloidal solutions in water. Qualitative evidence indicated the formation of a compound between manganese difluoride and titanium tetrachloride.

A reaction product corresponding to the formula $TiNCl \cdot TiCl_4$ was obtained by passing the vaporized tetrachloride in a current of nitrogen through a silent electric discharge at 4500 volts.[63] One per cent titanium nitride was formed. With traces of oxygen present, the product contained this component but no nitrogen, and appeared to be a mixture of oxychlorides. On adding a solution of the tetrachloride in chloroform to NOCl in the same solvent, a material corresponding to the chemical formula $TiCl_4 \cdot 2NOCl$ was formed.[64]

At low temperature the tetrachloride reacted with liquid hydrogen sulfide to form a compound corresponding to the formula $2TiCl_4 \cdot 2H_2S$.[65]

The solubilities of tantalum chloride ($TaCl_5$) and columbium chloride ($CbCl_5$) in titanium tetrachloride at 25° C. were found to be 14.3 and 0.24 per cent by weight; at 50° C. the values were 27.1 and 0.58 per cent; and at 100° C. they were 33.9 and 1.32 per cent, respectively.[66]

The liquid-vapor curves of titanium tetrachloride with carbon tetrachloride, silicon tetrachloride, and tin tetrachloride, showed no maxima or minima.[67] A study of the freezing-point curves revealed that the system titanium tetrachloride-silicon tetrachloride yielded an eutectic mixture containing almost 100 per cent of the latter, which solidified at −66° C. Carbon tetrachloride and antimony pentachloride yielded eutectics which contained 40 and 60 per cent titanium tetrachloride and solidified at −66° and −50° C., respectively. Stannic chloride formed a solid solution.[68]

TRICHLORIDE. Billy and Brasseur [69] found that titanium trichloride was best prepared by the action of powdered antimony (obtained by reducing solutions in hydrochloric acid with zinc) on the tetrachloride at 340° C. Any unreacted tetrachloride was removed from the product by washing with carbon tetrachloride, and antimony trichloride was washed out with ether. All operations were carried out in an atmosphere of carbon dioxide, with absolute

exclusion of air. Sodium amalgam reduced the tetrachloride to dichloride, but some trichloride was formed by reaction between these components. At slightly elevated temperature the titanic chloride was reduced to the trichloride by aluminum, magnesium, zinc, hydrogen, arsenic, and tin. Aluminum chloride catalyzed the reaction, and in the presence of this agent the reduction was quantitative at 200° C.[70] By carrying out the reduction with metallic silver in a sealed tube at 180° C., the trichloride was obtained along with silver chloride.[71]

Anhydrous titanium trichloride was obtained by reducing the tetrachloride with hydrogen at 600° C. [72] The product was a crystalline solid, black in reflected light and violet in transmitted light. By further heating the reactants at 660° C. in an atmosphere of hydrogen, a mixture of di- and tetra-chlorides was obtained.[73] According to Georges and Stahler,[74] at 1200° C. there was 94 per cent conversion to the violet crystalline trichloride.

Bock and Moser [75] prepared brown and violet varieties of titanium trichloride; the former could be converted into the latter form but the reverse was not true. Heat of solution of the brown type was higher than that of the violet. As a result of this work the compound was considered to be polymorphous. At 400° C. the violet type was produced by the action of a silent electric discharge on a mixture of titanium tetrachloride and hydrogen.[76]

Crystalline titanium trichloride of the chemical composition $TiCl_3 \cdot 6H_2O$ was prepared by electrolytic reduction of a 25 per cent solution of titanic chloride, followed by evaporation under reduced pressure at 60° to 70° C. to a specific gravity of 1.5, and cooling.[77] Such solutions can be obtained by dissolving the tetrachloride in water, or by dissolving titanium hydroxide in hydrochloric acid and reducing with zinc, iron, or similar agents, but obviously these materials would introduce impurities. Metallic titanium in the presence of hydrochloric acid reduced the aqueous tetrachloride almost wholly to the trivalent state.[78] Dilute sulfuric acid catalyzed the reaction.

Titanium trichloride oxidizes slowly in the air at ordinary temperatures, and at 440° C. decomposes into the tetrachloride and dichloride. It is soluble in water to form stable solutions which act as strong reducing agents. The rate of oxidation in aqueous solutions,[79] as determined from the velocity of oxygen absorbed at 30° C., was a linear function of the oxygen partial pressure and varied inversely as the concentration of free hydrochloric acid in the solution. Hydrolysis and complex formation largely influenced

the rate. The trichloride reacts with conjugated double bonds in organic compounds to give colored products,[80] although only ethylenic linkages next to ($=C=O$) groups are reduced by the reagent in ammoniacal solutions. It was particularly effective in reducing flavanones and flavones.[81] At low temperatures it combined with ammonia to give $TiCl_3 \cdot 6NH_3$, which reacted violently with water.[82] The latter product gave off ammonia at 300° C. and yielded a black product, probably $TiCl_3 \cdot 2NH_3$, which reacted so violently that it caught fire on exposure to moist air.

Solutions of titanium trichloride and tribromide gave absorption maxima at the wave length of 7440 Ångstrom units.[83] From a study of specific rotation of titanous ion near its absorption region, the existence of a doublet structure was found by Bose.[84]

DICHLORIDE. Titanium dichloride may be produced by reducing the tetrachloride in a current of hydrogen at 700° C., although at higher temperatures, 800° to 900° C., the metal is obtained.[85] Three reactions are involved in the reduction, $TiCl_4 + H_2 \rightleftarrows TiCl_2 + 2HCl$, above 600° C.; $TiCl_2 + TiCl_4 \rightleftarrows 2TiCl_3$, at 400° C. in a current of hydrogen; and $2TiCl_3 + 2HCl \rightleftarrows 2TiCl_4 + H_2$.[86] Schmidt[87] concluded that the dichloride could not be obtained as such by this method, because of the side reactions, but that it was always mixed with other products of the reaction, $2TiCl_2 \rightleftarrows Ti + TiCl_4$ and $TiCl_2 + TiCl_4 \rightleftarrows 2TiCl_3$. At 600° C. the tetrachloride was completely decomposed, but there was 82.6 per cent loss of titanium dichloride by sublimation. At 800° C. only a 0.4 per cent yield was obtained.

Anhydrous titanium dichloride, prepared by the thermal decomposition of the trichloride, decomposed slowly on heating in vacuum at 475° C., but was not volatile at 300° to 600° C. It reacted with ammonia at low temperature, giving gray $TiCl_2 \cdot 4NH_3$, which decomposed in air and dissolved in water with the evolution of hydrogen.[88] Titanium monoxide dissolved in hydrochloric acid with the evolution of hydrogen, but gave only 10 to 18 per cent yield of the dichloride.[89] Solutions of the dichloride were unstable and readily changed over to the trichloride.

Titanium dichloride may also be prepared by reduction of the tetrachloride with sodium amalgam, and by dissolving the metal in hydrochloric acid.

The magnetic susceptibilities of titanium dichloride, dibromide, and diiodide showed deviations from pure ionic magnetism.[90] These deviations were attributed to the type of atom bindings between the metallic ions.

The dichloride is a black solid, unstable in air. It dissolves in water, with the liberation of hydrogen, and gives a black precipitate with ammonia, which is oxidized slowly in air.

MONOCHLORIDE. According to Gallais [91] titanium monochloride shows marked absorption in the ultraviolet, with well-marked bands. The constitution of the solid is similar to that of the vapor, indicating that it is a homopolar rather than an ionic compound.

Fluorides

In addition to the characteristic di-, tri-, and tetra-valent salts, titanium forms a number of complex and basic fluorides.

The normal tetrafluoride may be obtained by the action of fluorine or anhydrous hydrofluoric acid on metallic titanium at elevated temperatures. Anhydrous hydrofluoric acid and antimony tetrafluoride react separately with the tetrachloride to form this compound. The product obtained by dissolving titanium dioxide in aqueous hydrofluoric acid is probably fluotitanic acid, although evaporation of such solutions at gentle heat results in a syrupy liquid which gives crystals of the tetrafluoride.

On heating titanium dioxide compounds with hydrofluoric acid or ammonium fluoride, a compound is formed which by further heating evolves titanium tetrafluoride or titanium diaminotetrafluoride, depending on the agent used. These reactions are involved in a process for pigment manufacture.[92]

FLUOTITANATES. Potassium fluotitanate, K_2TiF_6, can be prepared by the action of potassium hydrogen fluoride on a solution of titanium dioxide in an excess of concentrated hydrofluoric acid. The hydrated salt, $K_2TiF_6 \cdot H_2O$, may be crystallized from the solution obtained, either by adding potassium hydroxide to aqueous hydrogen titanofluoride or by fusing titanium dioxide in potassium carbonate and dissolving the melt in dilute hydrofluoric acid. The analogous sodium salt is prepared in a similar manner. Ammonium fluotitanate may be crystallized from the solution obtained by adding ammonium hydroxide to aqueous titanium tetrafluoride in a proportion just short of that required to yield a precipitate.

Fluotitanates of the alkaline earth and certain of the heavy metals have been prepared and crystallized in the hydrated form.

Titanium tetrafluoride is a white solid at ordinary temperatures; it has a specific gravity of 2.80 at 20° C. and a boiling point of 284° C. It dissolves in water to form clear solutions from which

the dihydrate, $TiF_4 \cdot 2H_2O$, may be crystallized. Titanium tetra-fluoride differs from the other tetrahalides in that it does not hydrolyze in aqueous solution on heating or on dilution. It absorbs ammonia, forming at low temperatures titanium triaminotetra-fluoride, $TiF_4 \cdot 4NH_3$, and at 120° C. the diaminotetrafluoride, $TiF_4 \cdot 2HN_3$, which are decomposed by hot sulfuric acid to give the dioxide.

According to Natta,[93] the tetrafluorides of titanium, silicon, and carbon give excellent X-ray photographs which show that these compounds crystallize in the cubic or tetragonal system.

From an investigation of ammonium hexafluorides of titanium, Hartmann [94] found that titanium tetrafluoride begins to distill off above 150° C. By electrolytic reduction of a solution of normal titanium fluoride containing ammonium fluoride, Piccini [95] obtained a violet crystalline precipitate of $TiF_4 \cdot 3NH_4F$ that was slightly soluble in water. The whole of the titanic acid content was precipitated from solutions of ammonium titanofluorides, $TiF_4 \cdot 2NH_4F$, by adding an excess of ammonia.[96] Quinine titanium fluoride separated on mixing alcoholic quinine with a hydrofluoric acid solution of titanium hydroxide, and the strychnine salt was prepared in a similar manner by mixing a solution of strychnine in hydrofluoric acid with H_2TiF_6 in the proportion of 2 to 1.[97]

Oxyfluopertitanates, derivatives of titanium trioxide, are prepared by adding alkali or alkaline earth metal fluorides to solutions of titanium tetrafluoride after oxidation with hydrogen peroxide.

Titanium trifluoride is obtained as an insoluble violet powder by igniting potassium titanofluoride in a current of hydrogen and leaching the product with hot water, or by reducing potassium titanofluoride in solution with zinc and hydrochloric acid or sodium amalgam.

Fluotitanites have been obtained as violet precipitates by the reaction of metal fluorides with titanium trifluoride. For example, a violet precipitate of ammonium pentafluotitanite, $(NH_4)_2TiF_5$, is formed by adding a concentrated solution of ammonium fluoride to one of titanium trifluoride. The analogous potassium salt, K_2TiF_5, is obtained as a deep violet precipitate by adding potassium hydrofluoride to the liquor obtained by treating titanium trifluoride with water. It is sparingly soluble in water but dissolves readily in dilute acids and yields a precipitate with ammonia which is readily oxidized to titanic acid.

Existence of the difluoride does not seem to have been definitely established.

Bromides

TETRABROMIDE.   Titanium tetrabromide is obtained as an amber-colored, hygroscopic, crystalline solid by the action of bromine vapor on the heated metal or carbide or on a mixture of titanium dioxide and carbon at red heat.   It may also be produced by passing anhydrous hydrobromic acid into the tetrachloride at temperatures below the boiling point.   Young [98] heated an intimate mixture of titanium dioxide and sugar charcoal at 300° C. in a stream of carbon dioxide to remove all moisture and air, then bubbled the carbon dioxide through liquid bromine and raised the temperature to 600° C.   The compound had a specific gravity of 2.6, a melting point of 39° C., and a boiling point of 230° C.   It hydrolyzed readily in aqueous solutions to oxybromides, and finally to titanic acid and hydrobromic acid.   Basic salts corresponding to the formulas $Ti(OH)_2Br_2$ and $Ti(OH)_3Br$ have been reported.

Ammonium bromotitanate is obtained by mixing ammonium bromide with a solution of titanium tetrabromide in hydrobromic acid.   It is a dark-red, crystalline solid, less stable than the corresponding chlorotitanate.   The mixed halides, titanium dibromide-dichloride and monobromide-trichloride, are obtained by the action of bromine on titanium dichloride and trichloride, respectively, in regulated proportions.

Fritsch [99] observed a large negative magnetic rotatory power of titanium tetrabromide paralleling that of the tetrachloride.   The sample prepared from titanium tetrachloride and hydrobromic acid was a yellow, crystalline solid having a melting point of 39.5° C.   Seki [100] determined the vapor pressure near the melting point, and from the results determined the thermodynamic properties of the compound.

TRIBROMIDE.   Titanium tribromide has been obtained by the electrolytic reduction of the aqueous tetrabromide, and by the reduction of the tetrabromide with hydrogen.   The compound was reported to be unstable.

According to Young,[101] titanium tetrabromide gave the dibromide at 400° C. in vacuum.

Iodides

TETRAIODIDE.   Titanium tetraiodide can be prepared by passing iodine vapor over heated titanium metal, by passing dry hydriodic acid into the tetrachloride, and by passing a mixture of titanium

tetrachloride, iodine vapor, and hydrogen through a red-hot tube.

The compound melts at 150° C. and distills without decomposition at a temperature slightly above 360° C. It fumes in air and dissolves in water to form solutions which are readily hydrolyzed to basic salts and finally to titanic oxide and hydriodic acid. Fast [102] prepared the tetraiodide by the reaction, at room temperature, between iodine and a large excess of metallic titanium. At 180° C. pure tetraiodide distilled over and was condensed in a second bulb. However, by heating the compound and metallic titanium for 1 hour, the diiodide was formed. At 550° C. the latter compound had an appreciable vapor pressure and partially reconverted to the tetraiodide, according to the reaction $2TiI_2 \rightarrow Ti + TiI_4$.

From the vapor pressure curve for liquid titanium tetraiodide, a number of physical constants were determined.[103] The boiling point was reported to be 377.2° C.

TRIIODIDE. Titanium triiodide, as the corresponding bromide, can be prepared by the electrolytic reduction of a solution of hydrous titanic oxide in hydriodic acid, and may be crystallized as a violet hexahydrate, $TiI_3 \cdot 6H_2O$. It is also obtained by the reaction between the diiodide and tetraiodide, $TiI_2 + TiI_4 \rightarrow 2TiI_3$.

By heating the triiodide in a high vacuum above 350° C. the reaction may be reversed to yield the original products. The compound dissolves slowly in water to form stable solutions, and is readily oxidized on exposure to air with the liberation of hydriodic acid.

Titanium diiodide can be prepared by heating the tetraiodide in a current of hydrogen and mercury vapor, or by heating a mixture of the tetraiodide and titanium metal at 700° C. in a reaction bulb and collecting the vapor in a second bulb at 44° C. The compound is a black, hygroscopic solid, which readily oxidizes on exposure to the air, with the liberation of hydriodic acid. It reacts violently with water, with the liberation of hydrogen.

Periodic acid and its salts react with salts of titanium to form complexes.[104]

Nitrates

Nitrates are probably formed by dissolving hydrous titanic oxide or titanates (potassium titanate, barium titanates) in nitric acid. On evaporation, however, the solutions yield a basic salt, $5TiO_2 \cdot N_2O_5 \cdot 6H_2O$. Such solutions are readily hydrolyzed on heating or dilution to yield titanic oxide and nitric acid.

Phosphates

Titanic phosphates precipitated from aqueous solution by re-action between soluble phosphates and salts of tetravalent titanium are more or less basic and thus of variable composition, and, in general, more uniform products may be obtained by fusing the dioxide with alkali metal phosphates or phosphoric acid. Titanyl metaphosphate $TiO(PO_3)_2$ may be obtained by dissolving titanic oxide in fused sodium or potassium metaphosphate and slowly cooling the melt. With a large excess of potassium metaphosphate, octahedral crystals of $TiO_2 \cdot P_2O_5$ were formed. Octahedral crystals, assumed to have the composition $TiO_2 \cdot P_2O_5$, were prepared by dissolving hydrous titanic oxide in orthophosphoric acid at tempera-tures around that at which dehydration began.

On adding a large excess of ammonium hydrogen phosphate to a solution of titanic chloride at 100°C., a precipitate formed slowly,[105] which, after washing with hot 5 per cent aqueous ammo-nium nitrate and water was calcined, first in a closed and then in an open crucible. Analysis showed a weight ratio of titanium dioxide to titanium dioxide plus phosphorus pentoxide in the prod-uct of 0.5234. Hydrated basic titanic phosphate [106] may be precipi-tated in a granular, readily filterable and washable form, practically free from iron and other impurities, by adding gradually, with con-stant stirring, solutions of phosphoric acid or soluble phosphates to a solution of a titanic salt (sulfate or chloride), under carefully controlled conditions of concentration, free acidity, and tempera-ture. Concentration of the titanium sulfate should not exceed 5 per cent titanium dioxide, and the precipitation temperature should be 50° C. or higher. To hold in solution undesirable impurities, such as iron and chromium, it was necessary to have free acid present. The presence of chlorides favored the formation of a granular product. Composition of the precipitate corresponded to the for-mula $3TiO_2 \cdot P_2O_5 \cdot 6H_2O$.

For example, a solution of titanium, containing 1 to 5 per cent titanium dioxide and free acid equivalent to 8 to 15 per cent sulfur trioxide, was subjected to reducing conditions to convert the iron component to the ferrous condition and heated to 80° to 90° C. A solution of sodium phosphate was added gradually in a proportion sufficient to provide slightly more than 1 mole phosphorus pentoxide for each mole of titanium dioxide. Under these conditions practi-cally the whole of the titanium was precipitated in the desired form, and little excess phosphoric acid was necessary. The precipitate was

dried, calcined, and ground to give a white pigment of excellent hiding power.

In a similar process, nelsonite ore was heated with 80 per cent sulfuric acid [107] at 175° C., and the reaction product was dissolved in 1.2 parts of water. After separation of the insoluble residue, the solution was treated with scrap iron to reduce all iron salts to the ferrous state, and then cooled to remove ferrous sulfate by crystallization. The supernatant liquor was then boiled to effect precipitation of basic hydrous titanium sulfate-phosphate, which, after washing, was calcined at 815° C. to yield a product containing 72 per cent titanium dioxide, 26 per cent phosphorus pentoxide, and 2 per cent impurities having satisfactory pigment properties.

Titanic salts that are hydrolyzable only with difficulty, for use in dyeing, mordanting, tanning, and lake manufacture, were prepared by combining the hydrated oxide with phosphoric acid and an organic acid, oxalic, lactic, tartaric, in a proportion of 1 or more moles for each mole of the oxide.[108] Alternatively, such compounds were obtained by treating titanic phosphate with organic acids, and also by the reaction between acid-soluble titanium salts of organic acids with phosphoric acid. By all methods the compound could be recovered in crystalline form by evaporating the solution.

PYROPHOSPHATE. Barnes [109] prepared a soluble double pyrophosphate of titanium and sodium by double decomposition from solutions of sodium pyrophosphate and basic titanium sulfate. According to Levi and Peyronel,[110] the pyrophosphate has a cubic form with 4 molecules in the cubic cell. The lattice constant was found to be 7.80 Ångstrom units, and the value of d was calculated as 3.106 Ångstrom units.

TITANOUS PHOSPHATE. The blue or purplish phosphate of trivalent titanium may be produced by the reaction between a soluble phosphate and a titanous salt (sulfate, chloride) in aqueous solutions. It is soluble in water, and the solutions are relatively stable toward hydrolysis.

Sulfides

A number of sulfides of titanium, in addition to the characteristic di-, sesqui-, and mono- compounds, have been described in the scientific literature.

DISULFIDE. The disulfide can be obtained by heating a mixture of rutile, sodium carbonate, and sulfur, by the vapor phase reaction between titanium tetrachloride and hydrogen sulfide, by the action

of hydrogen sulfide on titanium tetrafluoride, and by passing carbon disulfide over red-hot titanic oxide. It is stable in air at ordinary temperatures, but burns at elevated temperatures to titanium dioxide and sulfur dioxide. The heated compound is readily decomposed in a current of steam to yield hydrogen sulfide, sulfur, hydrogen, and titanic oxide. It dissolves in hydrochloric and sulfuric acids, with the evolution of hydrogen sulfide. In appearance it resembles mosaic gold.

SESQUISULFIDE. Titanium sesquisulfide, Ti_2S_3, is formed by igniting the disulfide in a current of an indifferent gas or by passing a mixture of moist hydrogen sulfide and carbon disulfide over titanium dioxide heated to bright redness. It is a grayish black, crystalline solid, stable in air, insoluble in dilute acids, but soluble in concentrated nitric and sulfuric acids with decomposition.

MONOSULFIDE. The monosulfide, TiS, can be obtained by heating the higher sulfides, di- and sesqui-, in a current of hydrogen or passing titanium tetrachloride over a heated tungsten filament. It is a reddish solid of metallic appearance, stable in air at ordinary temperatures, but glows on heating and yields sulfur and titanium dioxide. It is not affected by water or dilute acids, but dissolves in concentrated sulfuric acid.

Picon [111] prepared four sulfides of titanium, Ti_3S_4, Ti_4S_5, Ti_3S_5, and Ti_2S_3, under nonaqueous conditions at high temperatures, and studied their properties. The first of the group, Ti_3S_4, was obtained by heating titanic oxide with graphite in an atmosphere of dry hydrogen sulfide at 1650° C. This, in turn, yielded Ti_4S_5 on heating in vacuum beginning at 1300° C., and at 1400° C. in an atmosphere of dry hydrogen sulfide gave Ti_2S_3. By heating Ti_3S_4 at 800° C. for 1 hour in dry hydrogen sulfide, Ti_3S_5 was formed. Dry hydrochloric acid attacked the sulfides, Ti_3S_5, Ti_2S_3, Ti_3S_4, and Ti_4S_5, at 220°, 200°, 250°, and 315° C., respectively. Chlorine attacked all at 175° C. Aqueous hydrochloric acid gave no more than traces of hydrogen sulfide with any of the compounds at room temperature, and at 100° C. only Ti_3S_5 showed rapid liberation of this gas. Above 800° C. hydrogen sulfide, or a mixture of sulfur and hydrogen, slowly transformed the lower sulfides to Ti_3S_5. Water reacted slowly at 250° C. to form hydrogen sulfide, titanium oxide, and basic sulfates. Sulfur dioxide combined with the sulfides, Ti_2S_5, Ti_2S_3, Ti_3S_4, and Ti_4S_5 at 185°, 205°, 210°, and 225° C., respectively, but the reaction became appreciable only at 300°, 400°, 400°, and 400° C., and, as before, sulfur, titanium

oxide, and basic sulfates were formed. At 1000° C., anhydrous ammonia yielded a mixture of sulfides and titanium nitride. Concentrated nitric and hot sulfuric acids attacked all the sulfides; the latter yielded $Ti_2(SO_4)_3$. The speed of the reaction with hot sodium hydroxide solutions increased with the sulfur content of the compound. Aqueous potassium permanganate slowly converted the sulfides to potassium sulfate and titanium oxide.

The dioxide reacted with zinc sulfide and carbon to form a sulfide of titanium which volatilized only at high temperatures.[112] Sulfur reacted directly with titanium metal at high temperatures.

Compounds of Nitrogen

NITRIDE. Titanium has a strong affinity for nitrogen and burns in an atmosphere of the gas at 800° C., with incandescence, forming the hard, bronze-colored mononitride, TiN. This compound may also be formed by heating titanic oxide very strongly in the electric furnace in the presence of nitrogen, or by heating the dioxide for 6 hours at 1400° to 1500° C. in a stream of ammonia gas. It has a specific gravity of 5.18. It is hard enough to scratch rubies and slowly cut diamond. Freidrick[113] reported that titanium nitride was stable at its melting point, 3200° A., and that the electrical resistance at ordinary temperatures was 1.8 ohms per square millimeter.

The nitride of quadrivalent titanium, Ti_3N_4, may be obtained by the successive action of liquid ammonia and potassamide on the compound $TiBr_4 \cdot 8NH_3$, or by heating the compound $TiCl_4 \cdot 4NH_3$. It is also reported to have been prepared by burning titanium metal in an atmosphere of nitrogen. The compound is a copper-colored, hard, crystalline solid. According to Ruff and Eisen,[114] however, titanium nitride of formula Ti_3N_4 was found to consist of impure titanium mononitride with the oxide and TiNCl, and by strong heating in a stream of ammonia this product was converted to pure titanium nitride, TiN.

Bosch[115] prepared nitrides of titanium by heating a mixture of a titanic compound, carbon, and alkali metal salt, such as sodium sulfate or potassium carbonate, in a current of nitrogen at comparatively low temperatures. The alkali metal compounds acted as nitrogen carriers. As an example, a mixture of 80 parts titanic acid, 20 parts wood charcoal, and 2 parts sodium sulfate was heated in contact with nitrogen at 1240° C. Titanium nitride, as well as other nitrides or cyanonitrides, were formed.

By passing vaporized titanium tetrachloride in a current of nitrogen through a silent electric discharge at 4500 volts, about 1 per cent titanium nitride was formed, along with a compound corresponding to the formula $TiNCl \cdot TiCl_4$.[116] The compound was also formed by heating a charge of 40 parts titanium dioxide, 10 parts sodium carbonate, 10 parts lampblack, and 40 parts iron filings at 1000° C. in the presence of nitrogen.[117] A hydrocarbon gas or vapor, e.g., benzene, gasoline, or kerosene, may be used to replace part of or all the lampblack. A crystalline [118] structure was developed by heating the regularly prepared powder in an electric arc. The material had a specific gravity of 5.18; was harder than quartz; had high mechanical strength and was resistant to sudden changes in temperature. Purification [119] was effected by heating the initial product in air at 700° C. to burn out any carbon and then treating with sulfuric or hydrochloric acid and ferric chloride to dissolve silicides, phosphates, and sulfides without decomposing the nitride to form ammonia.

Rossi [120] proposed the use of titanium nitride in fertilizer as a source of nitrogen. Von Bichowsky [121] produced titanium nitride or cyanonitride for use as fertilizer or in the manufacture of ammonia by heating ilmenite or the purified oxide with carbon and sodium carbonate in proportions less than required for complete conversion to titanate at 1100° C. in an atmosphere of nitrogen.

The copper-colored crystals found in interstices of the lining bricks of a blast furnace corresponded to approximately 6 parts TiN and 1 part TiC.[122]

CYANONITRIDE. Titanium cyanonitride may be prepared by heating to whiteness a mixture of titanium dioxide and charcoal in a stream of dry nitrogen gas; by heating potassium ferrocyanide and titanic oxide in a closed tube to a temperature above the melting point of nickel; or by fusing potassium cyanide in contact with vapors of titanium tetrachloride. It is also formed in blast furnaces smelting titaniferous iron ores, and may be produced by heating a mixture of titanium dioxide and carbon in air at high temperature. The compound is a hard, copper-colored, crystalline solid, often appearing iridescent, having a specific gravity of 5.28, and possessing a metallic luster. In fact it was mistaken for a metal by early investigators. It is attacked by nitric and hydrofluoric acids, and the ignited material decomposes in a current of steam, yielding hydrocyanic acid, ammonia, hydrogen, and titanium dioxide. Chlorine reacts with the cyanonitride at red heat to form the tetrachloride. On a commercial scale,[123] cyanides of titanium, $TiCN_2$

or TiC_2N_4, can be made by heating a mixture of titanic oxide with an excess of carbon in contact with nitrogen at 1800° C. under a total pressure of 2 atmospheres. The partial pressure of carbon monoxide evolved was kept below 200 mm. of mercury. Carbon may be supplied by coke, coal tar, or pitch. Ammonia may be obtained by treating the cyanide with steam.

In 1849 Wohler [124] concluded that the copper-colored crystals so often observed in blast furnaces were not simple bodies but cyanide and nitride of titanium. Dry chlorine reacted with the crystals at elevated temperatures to form titanium tetrachloride. On passing steam over the crystals heated to redness in a porcelain tube, ammonia, hydrocyanic acid, and hydrogen were set free, leaving titanium dioxide of the anatase crystal form. Later Rudge and Arnall [125] reported these copper-colored crystals to be titanium nitride in admixture with carbon. Graphite and yellow crystals of titanium nitride were produced by passing chlorine over this blast-furnace product. Titanium oxychloride, $3TiCl_4 \cdot TiO_2$, as yellow crystals, was obtained by passing chlorine over the titanium nitride, with the introduction of moisture.

Von Bichowsky [126] found that nitric acid reacted with titanium nitride to form the dioxide and nitrogen gas. Sulfuric acid and sodium nitrate in aqueous solution reacted violently and evolved copious brown fumes of oxides of nitrogen. By adding the nitrate solution slowly and keeping the system cool, however, titanium sulfate was formed and a part of the nitrogen was converted to ammonia. Thus nitric acid alone, or in the presence of water and sulfuric acid, can completely oxidize titanium nitride to titanium oxides or sulfates and the nitric acid is at the same time reduced to nitrogen, nitrogen oxides, or ammonia. Higher recovery of combined nitrogen was obtained from the cyanonitride, Ti_5CN_4.

For example, 1 part sulfuric acid, 1 part sodium nitrate, and 0.1 part phosphoric acid were added to 1 part crude titanium cyanonitride suspended in 20 parts of water and the mixture was heated at 80° C. for 24 hours. More water was added to complete the precipitation of titanium oxide, and ammonium sulfate was recovered from the liquor. The titanium dioxide obtained was soft, fine grained, and of high purity.

In a similar manner, pure titanic acid was obtained by the action of sulfuric acid and sodium nitrate on the nitride Ti_2N_2 at 50° to 60° C.[127] The yield of ammonium compounds as by-products in the decomposition of titanium nitride or cyanonitride with nitric acid in the presence of sulfuric acid was increased by the action of

a phosphate compound,[128] which also catalyzed the oxidation reaction.[129]

Ammonia was also prepared from titanium nitride and cyanonitride by heating the material with an acid or a salt which splits off acid under nonoxidizing conditions, or by heating these compounds with steam in the presence of an agent which serves as an oxygen carrier.[130]

Guignard [131] treated titanium-nitrogen compounds with water vapor at a temperature of 360° to 500° C. and removed the ammonia or cyanide compounds from the reaction zones as fast as formed. By heating titanium nitride (Ti_3N_2) with a halogen oxyacid (HOCl) and sulfuric or phosphoric acids, titanium dioxide and the corresponding ammonium salt were formed.[132]

In 1862 Riley [133] prepared hydrous titanium oxide by oxidizing the nitride in a mixture of nitric and hydrochloric acids. The crude material was washed and fused with potassium bisulfate, the melt was dissolved in water, and the solution was boiled to effect precipitation. The hydrous oxide obtained could not be washed free of sulfuric acid, but none was detected in the calcined product. Farup [134] developed a process of preparing titanic oxide from titanium-nitrogen compounds in which the nitrogen was also recovered in usable form. By heating such compounds with concentrated sulfuric acid, the nitrogen was transformed to ammonium sulfate. At higher temperatures corresponding to superatmospheric pressure, comparatively dilute sulfuric acid could be employed to advantage. Titanium sulfate formed dissolved in the solution and was immediately hydrolyzed, almost quantitatively, and the sulfuric acid liberated again took part in the reaction so that only a negligible amount of acid was required over that necessary to combine with the nitrogen and possible impurities.

In an example, titanium nitride, prepared by reduction of ilmenite in an electric furnace in the presence of nitrogen, was treated with dilute acid to remove most of the iron and some of the silicates. One part of this product, containing 54 per cent titanium dioxide, 10 per cent nitrogen, and 5 per cent iron, was mixed with 1.33 parts by weight of 50 per cent sulfuric acid and heated in an autoclave for 3 hours at a pressure of 25 atmospheres. At the end of this period the reaction product was filtered and washed. The precipitate, which consisted of 85 per cent titanium dioxide, 2 per cent nitrogen, 0.5 per cent iron, and 5 per cent sulfuric acid, represented practically all the titanium of the original material, while the solution contained the remainder of the nitrogen in the form of ammonium sulfate,

together with some iron sulfate and free sulfuric acid. Titanium pigments and other titanium compounds were prepared from the residue by further treatment, according to conventional methods. If necessary, the titanium content was dissolved in strong sulfuric acid and reprecipitated.

A process for recovery of titanium dioxide from ores, combined with fixation of atmospheric nitrogen, was developed by Andreu and Paquet.[135] Ilmenite, rutile, or titaniferous iron ore was mixed with charcoal and sodium carbonate and heated in an atmosphere of nitrogen up to 1850° F. This product was then treated with steam at a temperature not exceeding 1800° F. to liberate ammonia, leaving a residue which was washed to obtain a titanate. From this, titanic oxide was recovered by hydrolysis or by treatment with dilute acid.

Alternatively, if it was not required to recover titanium dioxide, the ore was mixed only with carbon and heated in nitrogen to effect the fixation. The product was then treated with steam to split off ammonia, and the residue was used again.

In a related process,[136] ilmenite was mixed with a reducing agent and heated in an atmosphere of nitrogen in an electric furnace at 1200° to 1400° C. to form titanium nitride and metallic iron. If the charge included carbon, titanium cyanonitride was also formed. The iron was removed by magnetic separation or dissolved selectively by dilute acid, and the residue was heated with strong sulfuric acid to form titanium and ammonium sulfates. These compounds were dissolved in water and the solution was boiled to cause hydrolytic precipitation of titanium oxide, which also contained a small proportion of sulfuric acid. The filtrate was either evaporated to cause the ammonium sulfate to crystallize or heated with calcium hydroxide to liberate ammonia. After washing, the precipitate was treated with barium chloride and calcined to give a pigment consisting of titanium dioxide and barium sulfate. Alternatively, the product obtained after treatment with strong sulfuric acid was held at 400° C. to precipitate titanium dioxide, which was then washed free of iron.

Carbides

Moissan,[137] one of the first to prepare titanium carbide, fused titanic oxide and silicon carbide together in an electric furnace. Other methods involve heating titanium dioxide with carbon at 1700° to 2000° C. and fusing the dioxide with calcium carbide in the electric furnace. Ridgway[138] heated a charge of titania and

carbon in a closed electric resistor furnace having a graphite core and a steel casing. The reaction took place at 1600° to 1800° C., and as it proceeded an enlarged ingot of the carbide was progressively formed. An atmosphere free from oxygen and nitrogen, such as carbon dioxide from the reactant, was maintained throughout the reaction and until the product cooled.

Similarly, compressed masses of a mixture of carbon and titanium-iron alloy were heated to 1800° C. in an inert atmosphere to effect conversion to the carbide, and the crude product was purified by treatment in turn with hydrochloric and hydrofluoric acids, followed by removal of loose graphite after each treatment by a flotation process.[139] Parker [140] obtained carbides by heating finely divided titanium or titanium-iron alloy with a carburizing mixture of charcoal, manganese dioxide, potassium hydroxide, and ammonium chloride in a hermetically sealed box at 1800° C.

The carbide may also be made directly from ores.[141] Rutile was heated with the calculated amount of carbon to a high temperature, under reducing conditions, to form a plastic mass which was finally sintered. Fluxing materials were added to the charge if required. Carbides prepared in this manner contained impurities from the ores and unreacted charge. Graphite was removed by heating at a temperature below the melting point of the hard alloy to form the corresponding carbide, which was readily leached out by treatment with acid.[142] Crystalline titanium carbide [143] and metallic iron may be obtained by heating an equal mixture of ilmenite and coke in a carbon container in an electric resistance furnace. Iron was recovered as a by-product. According to Meerson,[144] titanium carbide forms at a much lower temperature in the presence of tungsten. Ballhausen [145] pressed into shape an intimate mixture of titanium dioxide with carbon black, coke, or graphite, and heated by resistance offered to the passage of an electric current to form the metal carbide.

The reaction produced by electrically heating a carbon filament in titanium tetrachloride vapors was followed by observing the change in resistance of the wire and by X-ray studies.[146] Titanium carbide (TiC) was formed, but to produce the pure compound the reaction product was heated either in a hydrocarbon atmosphere or in a vacuum. The final product was in the form of a hollow tube.

Titanium carbide is a crystalline solid of specific gravity 4.25, melting at 3410° C. Water and hydrochloric or sulfuric acids have no action even at 600° C., but it is attacked by aqua regia and burns in oxygen at red heat. Mott [147] estimated the boiling point to be

4300° C. It crystallizes in the cubic class of the isometric system, sodium-chloride type, with an *a* value of 4.3 Ångstrom units.[148] The compound forms a complete series of mixed crystals with vanadium carbide.[149]

Titanium carbide prepared by heating a mixture of titanium dioxide and carbon at 1200° to 3000° C. had a cubic lattice with a parameter of 4.26 to 4.31 Ångstrom units.[150] A sample, prepared by heating the dioxide and carbon in an electric furnace in an atmosphere of hydrogen at 1700° C., was a gray powder of metallic appearance with melting point about 3430° C. It was soluble in aqua regia. The specific resistance at room temperature was found to be 1.8 to 2.5 ohms, and at the melting point 7.0 ohms.[151]

Carbonization of titanium was studied at 1900° C. by heating the dioxide with carbon in an atmosphere of carbon monoxide and hydrogen.[152] Maximum saturation of the carbide by carbon (19.5 per cent carbon) occurred in the beginning of the process, and the value for bound carbon gradually dropped to 17 per cent. Treatment in the presence of nitrogen, such as would be possible under factory conditions, led to the formation of the nitride as a result of carbon displacement. For the preparation of pure titanium carbide, vacuum carbonization was necessary.

Naylor [153] measured the heat content of titanium carbide and nitride from 373° to 1735° K., calculated the entropies, and developed specific heat and heat capacity equations.

Higher carbides [154] corresponding to the chemical formulas TiC_2 and TiC_4 were prepared by heating titanium oxide with carbon under a total pressure of 2 atmospheres or more, while the partial pressure of the evolved carbon monoxide was maintained below 200 mm. of mercury.

Kinzie and Hake [155] reported a friable, amorphous, reactive compound of the chemical formula Ti_2OC_2, prepared by heating a mixture of rutile and carbon enclosed in an insulated mixture of coke, sand, and sawdust, in an electric resistance furnace without fusion.

A hard intermetallic, crystalline compound, corresponding to the chemical formula $TiWC_2$, was formed by heating a mixture of tungsten, titanium, and carbon for a prolonged period in a bath of molten nickel above 2000° C. in a graphite crucible.[156] On cooling, the compound was separated from the nickel by digestion, first with aqua regia and finally with hydrofluoric acid. These crystals had a hardness of 9.8 on Mohs' scale.

Kovalskii and Umanskii [157] made a study of the ternary titanium carbide-tungsten carbide-columbium carbide system.

Ferro- and Ferri-cyanides

The X-ray diffraction patterns of titanium ferrocyanide and titanium ferricyanide so closely resemble those of the corresponding compounds of iron, copper, cadmium, indium, aluminum, and zinc, with respect to the position and relative intensities of the diffraction lines, that it is concluded that these compounds form an isomorphous series having the same face-centered cubic symmetry.[158]

Hydrides

Archibald and Alexander [159] heated granular magnesium and titanium dioxide in an air-free atmosphere to produce metallic titanium, and then admitted hydrogen gas to the reaction zone to form the hydride. Klauber [160] obtained a good yield of titanium hydride by the discharge (spark) electrolysis of 0.1 to 0.2 normal sulfuric acid at a current density of 0.2 to 0.4 amperes and a potential of 240 volts, employing titanium electrodes, after a modification of the process developed by Paneth. The hydride was a colorless and odorless gas which burned in air with a colorless flame and deposited titanium dioxide. One gram of titanium absorbed 407 ml. of hydrogen [161] at room temperature, and 46 ml. at 1100° C., and at the lower temperature the hydride was formed.[162] The general behavior of the titanium-hydrogen system [163] was found to be analogous to that of the palladium-hydrogen system.

Titanium hydride is used in welding.[164] It is decomposed by heat in the zone of the weld to evolve nascent hydrogen and titanium as the molten metal which serves to facilitate the weld and improve its strength.

Titanates

Titanium forms an extensive series of titanates with the alkali, alkaline earth, and heavy base metals in which it appears as the acidic constituent. The more common members of the group, sodium, potassium, calcium, barium, magnesium, zinc, iron, nickel, cobalt, and lead, are usually prepared by heating the corresponding oxide, hydroxide, or carbonate, or in some cases neutral salts, with an intimate mixture of titanic oxide at elevated temperatures to bring about a direct reaction. With some of the stronger bases, however, the reaction may be effected in aqueous media. For example, barium and potassium titanate have been prepared by heating a suspension of hydrous titanium dioxide in a concentrated

solution of the corresponding hydroxide at the atmospheric boiling point.

Titanates of the alkaline earth and heavy metals are very stable compounds, insoluble in water, but are attacked slowly by acids. These compounds have been proposed for use as pigment, and they should be classed as potential pigments, although only lead meta-titanate, $PbTiO_3$, has been employed for this purpose on a commercial scale.

The alkali metal titanates, which are in general soluble in water and in dilute acids, are employed as intermediaries in preparing other compounds of titanium from ores. Potassium metatitanate, K_2TiO_3, may be formed by fusing titanium dioxide with potassium carbonate, and the tetrahydrate, $K_2TiO_3 \cdot 4H_2O$, by boiling a suspension of titanic acid in aqueous potassium hydroxide. The hydrated salt is very soluble in water. Sodium metatitanate and ortho-titanate can be prepared by fusing titanium dioxide with chemically equivalent proportions of sodium carbonate. The meso- and para-titanates have been reported. According to Washburn and Bunting,[165] the binary system, sodium oxide-titanium dioxide, forms compounds of the chemical composition Na_2TiO_3, melting at 1030° C., Na_2TiO_3, melting at 985° C., and $Na_2Ti_3O_7$, melting at 1128° C.

Sodium and potassium titanates, soluble in organic and dilute mineral acids, were prepared by heating hydrous titanic oxide with 1.6 to 2.0 parts of the corresponding hydroxide or carbonate at 100° to 200° C.[166] The white, crystalline, slightly hygroscopic solids were used for making other compounds of titanium. Similar compounds were obtained by Rockstroh[167] by heating dried titanic oxide with an alkali metal hydroxide or carbonate at 150° to 220° C. Titanates of the type $Na_2Ti_5O_{11}$[168] were produced by heating rutile or bauxite residues with alkali metal compounds such as sodium carbonate, sodium sulfate, potassium carbonate, and potassium hydroxide at 800° to 1000° C., in the ratio of 2 moles alkali metal oxide to 5 moles titanium dioxide. Coggeshall[169] heated rutile with anhydrous alkali metal carbonates at a dull red heat. Water-soluble compounds (titanates) were obtained by igniting titanic oxide with sodium carbonate in a directly heated rotary tube furnace.[170]

The mono- and di-titanates of lanthanum, praseodymium, neodymium, samarium, and yttrium have been prepared by fusing the corresponding oxide with titanium dioxide in stoichiometric proportions.[171] The samarium and yttrium compounds, $Sm_2Ti_2O_7$ and

$Y_2Ti_2O_7$, have a cubic crystal structure. Results generally paralleled those obtained with the corresponding silicates.

Barium titanate was prepared as an intermediary step in the conversion of anatase to rutile by boiling a suspension of acid-free hydrous titanic oxide in an equivalent amount of barium hydroxide solution.[172]

Pulp obtained from thermal hydrolysis of a sulfate solution of ilmenite was treated with dilute aqueous sodium hydroxide to neutralize the residual sulfuric acid, and the salts formed by the reaction were removed by further washing with water. A portion of this product, as a thick paste containing 80 g. titanium dioxide, was suspended in a solution of 315 g. barium hydroxide octahydrate, $Ba(OH)_2 \cdot 8H_2O$, in 2 liters of water and the mixture was boiled at atmospheric pressure for 1 to 2 hours to complete the reaction.

A solid solution of $7BaTiO_3 \cdot SrTiO_3$ showed at room temperature a tetragonal structure, but changed at 80° C. to the cubic type.[173] Around the transition point the two structures coexisted over an interval of several degrees. Barium titanate shows several specific heat anomalies.[174] At the Curie point, 120° C., there is a maximum in the heat capacity as a result of disappearance of the spontaneous polarization. Another anomaly occurs at 5° C. and coincides with the dielectric constant maximum.

Hedvall[175] obtained the metatitanate $CaTiO_3$, but no orthotitanate, by igniting at a high temperature an intimate mixture of titanium dioxide and calcium oxide. However, a study of the melting-point diagram[176] of mixtures of these oxides showed maxima at the composition corresponding to $CaO \cdot TiO_2$, $2CaO \cdot TiO_2$, and $3CaO \cdot TiO_2$, and eutectics containing 12 per cent calcium oxide at 1420° C. and 52 per cent at 1780° C. In a similar study,[177] various amounts of these components were heated for 10 hours at 1350° C. With equimolecular amounts of calcium oxide and titanium oxide, the compound $CaO \cdot TiO_2$ formed, but with calcium oxide in excess it formed a solid solution with the titanates. The crystal structure of the product, synthetic perovskite, was found to belong to the regular system, and the lattice constant was 7.61 Ångstrom units. According to Parga-Pondal and Bergt,[178] if calcium oxide was present in the system in equivalent proportion or in excess, the metatitanate formed at temperatures up to 1300° C., but at 1400° C. a compound corresponding to the formula $3CaO \cdot TiO_2$ was formed. Melting corresponding raw mixtures in the oxyacetylene flame indicated the existence of titanates rich in lime. In the presence of

silica there was no evidence of the formation of double compounds between calcium silicate and calcium titanate.

A titanite spinel [179] of the formula $MgO \cdot Ti_2O_3$ has been made by heating magnesium with titanium dioxide, metallic titanium with magnesium oxide, or titanic oxide with magnesium oxide under reducing conditions. The product was a violet to black crystalline solid. Tanaka [180] produced magnesium ortho-, meta-, and di-titanates by high temperature reactions between magnesium oxide and titanium dioxide. Calcium oxide and titanium dioxide yielded only one addition product, $CaTiO_3$, but formed solid solutions. The compound was sensitive to light.

Cole and Nelson [181] followed the reaction between mixtures of hydrous titanium dioxide and zinc oxide, ranging from 33 to 59 per cent of the former on the dry basis at temperatures between 400° and 1000° C., by determining the size of the unit cell of the product. Zinc orthotitanate was the only compound formed, but solid solutions of titanium dioxide in this compound were found to extend to the composition represented by the formula $Zn_2TiO_4 \cdot 5TiO_2$. These products were not stable at high temperatures and began to dissociate at 775° C. into titanium dioxide and another solid solution that was poorer in this component. The primary reaction was initiated at 430° C., and the formation of zinc orthotitanate was practically complete at 800° C. after 3 to 6 hours. A product corresponding to the composition of zinc metatitanate was found to be in reality a solid solution of titanium dioxide in zinc orthotitanate. The unit cell of the orthotitanate was determined by X-ray measurements to be 8.46 Ångstrom units, and the specific gravity of the pure compound was 5.12.

Cobalt and nickel metatitanates, corresponding to the chemical formulas $CoTiO_3$ and $NiTiO_3$, have been reported formed by fusing the corresponding chloride with titanium dioxide.

From X-ray data, Cole and Espenschied [182] found that the reaction between titanium dioxide and litharge, in proportions from 25 to 89 per cent of the latter component, yielded only one compound, lead metatitanate. Combination started at 360° C. and was completed at 400° C. in 4 hours. The samples for study were prepared by calcining an intimate mixture of litharge with hydrolytically precipitated titanic oxide pulp freed from sulfuric acid. Crystals were obtained by dissolving the product in sodium tungstate at 850° C. and cooling the melt. Such crystals were also obtained from a system rich in litharge. For instance, at 900° C. a charge of 2 moles lead oxide to 1 mole titanium dioxide gave a mixture of

crystalline lead titanate and molten lead oxide. Samples of lead titanate held for 24 hours at 400°, 575°, 700°, 775°, 860°, and 1000° C., and cooled in air, gave identical diffraction patterns, and a hard-sintered sample, held at 1200° C. for 2 hours, yielded the same pattern. No difference was observed in the products obtained, employing excess of either ingredient or of the crystalline material. The titanate crystallized from melts as orthorhombic holohedral pyramids. Nicholson [183] likewise made X-ray studies of the products obtained by calcining mixtures of titanium dioxide and litharge over a wide range of proportions at 700° C., and was able to detect only three crystalline phases, tetragonal lead monoxide, anatase, and lead titanate ($PbTiO_3$). Lines corresponding to the titanate were obtained consistently from the calcination products of other lead and titanium compounds, and were identical with those produced by the commercial pigment.

In a study of speeds of reaction, rhombic, yellow, lead monoxide and tetragonal, red, lead monoxide were mixed in equimolecular amounts with commercial titanium dioxide and heated in glass ampoules at 400° to 800° C.[184] Velocity of formation of lead metatitanate from the two oxides in air, nitrogen, and carbon dioxide did not vary greatly but was more pronounced at different temperature intervals. The yellow rhombic oxide reacted more rapidly below the conversion temperature, 488.4° C., and the tetragonal form more rapidly at higher temperatures.

Ferrous and ferric metatitanates, corresponding to the minerals ilmenite and arizonite, have been prepared synthetically from the appropriate oxides.

A study of the system Fe_2O_3-FeO-TiO_2 at high temperatures revealed that only rutile, iron glance, and pseudobrookite, Fe_2TiO_3, separated from the melt.[185]

Chapter 8

ORGANIC COMPOUNDS OF TITANIUM

Many organic compounds of titanium have been reported in the scientific literature, but few of these are of more than academic interest. The double potassium and titanium oxalate, $K_2TiO(C_2O_4) \cdot 2H_2O$, may be crystallized from solution, is quite stable toward hydrolysis, and is employed commercially in dyeing, mordanting, and tanning. Titanium is a constituent of a number of permanent metallized azo dyes. The phthalate has been mixed with regular titanium dioxide pigment to improve the resistance to chalking in outdoor service.

Titanium oxalate [1] soluble in water was obtained by treating titanium sulfate or a double alkali metal sulfate with oxalic acid or an alkali oxalate. The reactants may be intimately mixed in a solid or moist state or may be dried and heated together. In another modification,[2] titanium sulfate solution was added to a solution of a carbonate of an alkali metal or ammonium until a pH of 6 was reached, and this intermediary titanium carbonate compound was washed and gradually added to an aqueous solution of oxalic acid containing a small proportion of octyl alcohol which served to slow down the reaction. The precipitated titanium oxalate was filtered and washed. Basic titanic oxalate [3] may be obtained from solutions of tetravalent titanium in mineral acids by adding oxalate ions under regulated conditions of neutralization, dilution, and temperature. For instance, such a compound was precipitated by adding 0.15 to 0.30 mole oxalic acid or an equivalent amount of an alkali or alkaline earth metal oxalate to a solution containing 0.6 mole sulfuric acid and 1 mole of titanium dioxide. Such a solution was strongly basic. The temperature was held below 50° C., and the solution was diluted to effect precipitation. In the presence of chloride ions, precipitation may be effected from a more acid solution, thus yielding a purer product.

Titanium compounds soluble in organic and in dilute inorganic acids may be prepared by heating metatitanic acid or basic sulfate with an alkali below the fusing point, 150° C. By treating the reaction product with appropriate acids, double salts, such as titanium

sodium tartrate, lactate, and sulfate, and titanium potassium oxalate, were obtained.[4]

The complexity of titanium oxalates is proved by the ease with which they may be crystallized from solution and by their resistance to hydrolysis on dilution and heating, in contrast to other salts. Titanium sulfate gives an immediate precipitate with ammonium hydroxide which almost completely redissolves on addition of hydrogen peroxide. Thus it appears that the introduction of active oxygen into the titanic oxide molecule promotes the formation of complex ions. Pechard[5] reported that titanic acid prepared by the action of sodium carbonate on aqueous titanium tetrachloride dissolved readily in a warm solution of potassium acid oxalate, and on cooling a precipitate of crystalline titanium potassium oxalate formed.

In preparing double formates and double acetates in the form of water-soluble crystals, Stahler[6] added a saturated solution of an alkali, alkaline earth, or ammonium formate or acetate in excess to the concentrated solution of a salt of trivalent titanium (sulfate, chloride). The crystalline salt was separated from the liquor, with exclusion of air.

Fenton[7] obtained a bulky chocolate-colored precipitate on adding a warm aqueous solution of a quadrivalent titanium salt to a solution of dihydroxymaleic acid. Titanium tetrachloride reacts with high molecular weight monobasic organic acids, such as stearic and oleic, at 70° to 110° C., under anhydrous conditions, to form soaps which may be used as driers in paints and varnishes.[8] At the temperatures employed, the hydrochloric acid was eliminated as formed. Tartaric acid combined with titanium tetrachloride to form a complex[9] in which the two constituents were present in equimolecular amounts, while the hydroxide and sodium tartrate formed a similar product in which the mole ratio was 2 to 3.

A tervalent titanium compound, prepared by reducing alcoholic $(C_2H_5)_4TiO_4$ with sodium, had a dark blue color and dissolved in dilute hydrochloric and sulfuric acids to form the corresponding titanous salt.[10] Solutions obtained in this manner were entirely free of iron and other metallic or acidic impurities.

Titanium phthalate[11] can be made by adding titanium sulfate solution, adjusted to slight acidity, to an aqueous solution of sodium phthalate prepared by neutralizing phthalic acid or anhydride with sodium hydroxide in stoichiometric proportions. One mole of titanic sulfate reacted with 2 moles of sodium phthalate. A dense white precipitate formed which usually contained more or less

titanium hydroxide, depending on the degree of hydrolysis. On drying at 105° C., the washed precipitate became gelatinous and had a tendency to form semivitreous or horny aggregates resembling silica gel. The acidity of the titanium sulfate solution was an important factor. For instance, if highly acid solutions were employed, precipitation was delayed and the yield and composition of the product were frequently unsatisfactory. On the other hand, a practically neutral sulfate solution gave a precipitate containing an appreciable proportion of titanium oxide, with the result that the phthalate content was considerably less than normal. Basic titanium phthalate was produced by adding ½ mole proportion of aqueous sodium phthalate to a solution of titanyl sulfate.[12]

An aqueous solution of a titanium salt was added to a solution of a carbonate of an alkali metal or ammonium until a pH of 6 was obtained, and the precipitate, after thorough washing, was added to a water solution of oxalic acid containing a small proportion of octyl alcohol to obtain a basic titanium oxalate corresponding to the chemical formula $(TiO)_2(C_2O_4)_2$.[13]

In concentrated sulfuric acid, titanium dioxide gives complex compounds of various colors with hydroxy aromatic compounds such as phenol, salicylic acid, and metol.[14] These colored compounds have been suggested as a basis for the colorimetric determination of titanium. Titanium tetrachloride reacted with phenols in the presence of ammonia or organic basis in anhydrous media to form alcoholates and phenylates.[15] Employing higher alcohols, a lower alcoholate was made first and this compound was reacted with the higher alcohol. For example, titanium tetrachloride was mixed with ethyl alcohol, and ammonia dissolved in ethyl alcohol was added. Typical compounds of this class are titanium tetraethylate and tetraphenylate. Titanium tetrachloride added slowly to dry methyl alcohol gave the solid dimethyloxydichlorotitanium, and triethoxychlorotitanium was prepared by refluxing tetramethoxytitanium and acetyl chloride at 70° to 80° C. for 2.5 hours. Addition of ethyl alcohol gave a solid product containing ethyl alcohol of crystallization. Refluxing triethoxychlorotitanium with acetyl chloride, or titanium tetrachloride with ethyl alcohol, for 24 hours at 80° to 100° C. gave diethoxydichlorotitanium, a pale yellow solid. Crystals containing methyl and ethyl alcohols were obtained by adding the corresponding reagent. Diisopropoxydichlorotitanium was prepared by refluxing titanium tetrachloride in isopropyl alcohol for 9 hours. Diisobutoxydichlorotitanium was prepared in a similar

manner. These dichloro compounds were readily hydrolyzed in air and dissolved instantly in water, yielding clear solutions.[16]

McCleary[17] produced a water-soluble compound by heating titanium tetrachloride with a tertiary alcohol (butyl) which was used to prepare a slightly opalescent water solution containing more than 100 g. per liter titanium dioxide. $Ti(OPh)_4 \cdot PhOH$, obtained by heating the anhydrous tetrachloride with phenol, was an orange red crystalline powder soluble in organic solvents, but which decomposed slowly in water.[18] The dark red crystalline $TiCl_2(C_{10}H_7O_2)_2$, obtained by the reaction of the tetrachloride with 2-naphthol in dry carbon disulfide, was decomposed by moist air.

Titanium gluconate[19] may be prepared by the double decomposition reaction between an alkaline earth gluconate and aqueous titanic sulfate. After filtering off the alkaline earth sulfate formed, the gluconate was obtained as a greenish-yellow, syrupy liquid, and the solid compound was precipitated by adding an organic compound miscible with water. The purity of the titanium gluconate was found to depend in a large measure upon the relative proportions of titanium dioxide and sulfuric acid in the original solution. In general, a molecular ratio of 1 to 1 gave best results. In an actual operation, powdered calcium gluconate was added, with agitation, to a solution of titanyl sulfate. Reaction occurred at once, with the precipitation of calcium sulfate and the formation of a greenish-yellow, viscous liquid. Water was added to maintain the required fluidity, and, after the calcium sulfate had settled, the supernatant liquor was separated by decantation and filtration. Titanium gluconate was then precipitated from the solution by the addition of methyl alcohol. The washed and dried product was a white powder containing 28.7 per cent titanium dioxide and consequently represented almost pure gluconate.

Titanium alcoholates reduce aldehydes and ethers.[20] The reduction of titanium tetrachloride by alcohol is accompanied by autoxidation and formation of hydrogen peroxide. Reduction of mandelic or lactic acid was free from such complications, and in daylight or mercury arc proceeded with a speed proportional to the concentration of the reducing agent and of the tetrachloride.[21]

Organic titanic compounds may be prepared by treating titanium tetrachloride with aromatic hydroxyl compounds, such as phenol, in the presence of ammonia or an amine.[22] The reaction may be carried out in an inert solvent, such as benzene, and it may be initiated in the absence of and completed in the presence of the

organic base. Titanium tetrachloride reacted with phenol to form trichlorotitanium phenolate,[23] $TiCl_3OC_6H_5$, which readily hydrolyzed to give titanium hydroxide, phenol, and hydrochloric acid. The tetrachloride also reacted with para chlorophenol to form $TiCl_3(OC_6H_4Cl)_2$.[24] A precipitate of $(C_2H_5)_2COTiCl_3$[25] was formed by treating benzophenone in anhydrous benzene with titanium tetrachloride. Triphenylcatechol titanates have been separated into their optical isomers by the use of cinchonine.[26]

Demarcay[27] observed that titanium chloride combined with oxygenated ethers as well as with sulfides and sulfhydrates of alcohol radicals. Methyl ether combined with anhydrous titanium tetrachloride in molecular proportions at temperatures above 150° C. to give a yellowish, solid complex having the composition corresponding to the formula, $TiCl_4 \cdot CH_3 \cdot O \cdot CH_3$.[28] Titanic chloride and benzoic chloride combined directly to form a double chloride corresponding to the formula, $TiCl_4 \cdot C_6H_5COCl$.[29] Addition of titanium tetrachloride in chloroform to solutions of diphenyl ketone, heliotropin, and methyl phthalate in the same solvent gave precipitates of crystalline addition compounds which were unstable in moist air.[30] The oxonium salt, $TiCl_4 \cdot 2(C_2H_5)_2O$, formed by the reaction of titanium tetrachloride and anhydrous ethyl ether, was very hygroscopic and was readily decomposed by water.[31]

Complex compounds were produced by the reaction of isovitamin C, or its first reversible oxidation product, with an alkali, alkaline earth, or ammonium salt, and titanium tetrachloride in a medium consisting of one or more mono- or poly-hydroxy alcohols or ketones.[32] A basic compound of quadrivalent titanium for use in treating paper or leather was formed by the reaction in aqueous solution of titanium tetrachloride with a sulfamate of a metal which yields an insoluble chloride, such as lead.[33] 5 Chloro-2-furyl ethyl ketone may be prepared by the Friedel and Craft reaction of 2-nitrofuran, propionyl chloride, and titanium tetrachloride.[34] Titanium tetrachloride reacted with organic compounds of nitrogen to form complexes in which the ratio of the components was not generally accountable on the basis of a constant coordination number of 6 for titanium.[35] Para nitro- and 2-4 dinitrophenyl-hydrazones were reduced by titanium tetrachloride to $p-C_6H_5(NH_2)_2$ and 2-4 $(H_2N)_2C_6H_3NH \cdot NH_2$, respectively.[36] Titanium halides form crystalline binary complexes with nitrilles[37] and with nitro compounds.

Organo metallic compounds[38] may be prepared by treating titanium tetrachloride with eight mole proportions of a primary, sec-

ondary, or tertiary amine in an anhydrous solvent. Gilman and Jones [39] prepared compounds of this type from titanium tetrachloride, and studied their reactivity.

The reaction of isobutene with titanium tetrachloride at low temperature was induced by traces of moisture but was not affected by dry hydrochloric acid.[40] Methyl maltoside heptaacetate with ortho ester structure, on treatment with titanium tetrachloride, gave the normal acetochloromaltose and not the third acetochloromaltose from which it was prepared,[41] and ethyl tetraacetyl-β-d-glucosido-glucose was similarly converted to aceto chloroglucose.[42]

Rothrock [43] produced plastic molding and casting compositions by polymerization of esters of unsaturated alcohols with inorganic acids of titanium, such as methyl methacrylate titanate and tetramethallyl titanate. Interpolymers of tetramethallyl titanate and vinyl acetate gave white enamel-like surfaces that were resistant to wear.

The esterification of linseed-oil fatty acids with glyceryl titanate yielded oils of good drying properties but dark in color.[44] By heating butyl titanate with glycerol, a white solid glycerol titanate formed which was insoluble in water and in the common organic solvents. A reddish, viscous liquid, which in thin layers dried in air to give transparent, glassy, brittle films, was formed by refluxing phenyl titanate with formaldehyde in butyl alcohol.

Photoreactions. Fading of Dyes

Renz [45] found that titanium dioxide yielded dark-colored reaction products in the sunlight and in the presence of organic acceptors. Similarly, Williamson [46] noted that certain samples of titanium dioxide darkened reversibly on exposure to sunlight. Ceramic glazes prepared from these samples had similar properties. In some cases photosensitive glazes were prepared from materials which before combination did not show this phenomenon. This photosensitivity appeared to be a function of the source of the raw material from which the oxide was prepared. Ilmenite from Norway, for instance, tended to produce sensitive oxide. Extremely small proportions of certain metallic compounds as impurities, such as ferric oxide, aluminum oxide, and rubidium oxide, intensified this tendency.

According to Williamson,[47] the photoluminescence of impure rutile is probably connected with the entry of impurities, particularly iron compounds, into the crystals during calcination. For example,

a pure sample of nonphotosensitive titanium dioxide mixed with enough of an iron salt to add 1 part in 500 of ferric oxide, ground, and calcined for 3 hours at a final temperature of 1000° C., gave a product which exhibited reversible darkening in daylight.[48]

The photoactivity of titanium dioxide and other oxides in the presence of glycerin was studied by Renz, who showed that the titanium dioxide was reduced to the sesquioxide, while the glycerin was oxidized to aldehyde and acids.[49] A paint prepared from linseed-oil varnish and titanium dioxide pigment tinted with Prussian blue showed considerable bleaching after exposure to sunlight for 35 days. The effect could not be explained by the presence of residual sulfuric acid, for lithopone, which may develop acid on weathering, did not bleach Prussian blue.[50] Wagner[51] concluded, however, that such fading was caused by residual sulfuric acid. In some cases the bleaching was attributed to the formation of titanium sulfate, and in others to the trioxide. Addition of zinc oxide in proper proportions produced a stable pigment which did not bleach the dyes.

A series of paints in vehicles of 15 per cent dextrin solution alone, and mixed with 5 per cent glycerol, casein solution, and oil, and tinted with azo dyes which contained no sulfo group and also with some basic dyestuffs (madder lake K), was pigmented with titanium dioxide, zinc oxide, lithopone, and white lead. Films containing titanium dioxide faded more rapidly than the others on exposure to the sun or to ultraviolet light.[52] The bleaching by light of a powder made by dyeing titanium dioxide with "Chlorazal Sky Blue" was studied by Goodeve and Kitchener.[53] After an initial slow period, the quantum efficiency depended upon the concentration of vulnerable dye molecules.

Titanic oxide, sulfate, and chloride in alcohol or oxalic acid solution turned blue or brown slowly on exposure as a result of formation of simple or complex salts.[54]

Physiological Effects

A number of investigators have demonstrated experimentally that titanium compounds are not toxic.[55] The noninjurious effect of the dioxide was demonstrated by Heaton,[56] who within a short time ate a pound of commercial pigment, titanium dioxide-barium sulfate composite, mixed with a little glucose. Passage through the alimentary canal was observed by X-ray photographs and a fluorescent screen, and complete elimination required 24 hours. No

harmful effect was felt or detected, and on the contrary it apparently cured an ailment which had baffled physicians for years.

Titanic acid, along with silica and similar substances, has been detected in the lungs of patients suffering with silicosis and other lung diseases, although there was no indication that the titanium compound was responsible for the disease.[57] The dioxide, fed to various animals for a period of 6 months, proved harmless.[58] Daily ingestion by sheep of 2 to 3 grams showed no ill effects after 3 months, and complete elimination in the excreta suggested its application as a reference substance for digestion studies.[59] After feeding the compound to guinea pigs in considerable amounts, no ill effect was noted, only traces remained in the intestinal tract, and none was detected in other organs.[60]

Small doses of the double titanium and sodium tartrate increased the respiration rate in frogs, mice, and rats, and larger amounts caused paralysis and death.[61] Carteret [62] ascribed the toxicity of preparations of this type to the effect of the acid radical. Alkaline titanium citrates, lactates, and stearates were studied. Experiments in vitro showed that titanium trichloride markedly inhibited blood phosphate activity.[63]

The titanium complexes of ascorbic and dehydroascorbic acids have been successfully employed in the chemotherapy of cancer,[64] but they occasionally show toxic action. Pick [65] reported the use of the disulfide and the salicylate of titanium in the treatment of diseases of bacterial origin. These compounds were especially effective in lupus. Intermuscular injections of an olive-oil suspension of hydrous titanic oxide or titanocitrate into rats having Jensen sarcoma reduced the rate of mortality and checked the growths.[66] From a study of erythropoietic action of inorganic elements fed to anemic rats daily, along with 0.5 mg. of iron, Beard and Myers [67] found that recovery occurred in 2 to 3 weeks with the addition of 0.1 mg. of titanium, as compared with 4 to 6 weeks with iron alone.

Diseased skin areas treated with titanium dioxide ointment healed more quickly than untreated areas.[68] No irritation resulted on applying the dioxide to the skin of normal rabbits for 15 days. An ointment containing this agent was used during the first World War for the treatment of erythema caused by exposure to mustard gas.[69]

From the results of extensive studies, Kahone [70] concluded that the use of titanium dioxide and its derivatives in pharmacy and cosmetics was justified by the innocuousness of these compounds.

Growth and fermentation were accelerated by ascorbic acid com-

plexes of titanium.[71] According to Pick,[72] all soluble organic and inorganic compounds of titanium check the putrefaction of animal and vegetable proteins. Twenty grams of putrescent liquid was deodorized by addition of 0.1 g. titanium sulfate.

Hanzlick and Tarr [73] found titanium tetrachloride to be a severe skin irritant. Applications to the skin of dogs produced hyperemia, swelling and edema, ulceration and necrosis. Similar changes, together with vesication, took place on human skin.

Titanium compounds have been reported to act as catalysts in the oxidation reactions of vegetable cells, and there is evidence that the element is essential in the formation of soils from rocks.[74]

Chapter 9

METHODS OF CHEMICAL ANALYSIS OF TITANIUM COMPOUNDS

The literature on the analytical chemistry of titanium, which is very extensive, includes processes for its separation and determination, gravimetrically, volumetrically, electrometrically, and colorimetrically. Gravimetric estimations are generally based on the hydrolysis of dilute, weakly acid solutions by long boiling, or precipitation by special reagents such as "cupferron," the ammonium salt of nitrosophenylhydroxylamine, and tannic acid. Hydrolysis of quadrivalent salt solutions usually gives erroneous results because of the interference of aluminum, phosphoric acid, iron, chromium, and other substances which normally accompany titanium, particularly in ores. Titanic acid, precipitated by the slow process of thermal hydrolysis, frequently adheres to the surface of the glass vessel so tenaciously as to make complete removal practically impossible, and during the long period of boiling there is some solvent action on the glass, with the result that contamination inevitably occurs. Although this was the first method employed for the determination of titanium, in view of the many disadvantages it is now practically obsolete.

Cupferron is accepted as an excellent reagent for the precipitation of titanium, although ferric iron, copper, zirconium, thorium, tin, vanadium, and uranium are also precipitated quantitatively under favorable conditions. In addition, certain other elements, particularly silicon, tungsten, cerium, silver, lead, mercury, and bismuth, are known to be partially precipitated or more or less occluded with the titanium. Fortunately most of these may be separated by well-known methods before adding the cupferron, and besides, since comparatively few of these elements are commonly associated with titanium, the possibilities of serious interferences are not so great as might be supposed. The degree of acidity of solutions from which total precipitation may be effected varies widely with the different elements, and with titanium, iron, and zirconium it is unusually high. This property offers a means of at least partial separation. Iron is usually present in crude titaniferous materials in appreciable proportions, and its removal may be accomplished readily by precip-

itation with hydrogen sulfide from an ammoniacal solution containing also ammonium salts of certain hydroxy organic acids, particularly citric and tartaric, followed by filtration. Under these conditions titanium has the special property of remaining in solution. Solutions for analyses may contain almost any acid, and sulfuric in amounts up to 40 per cent by volume exhibited no solvent action on the precipitate, although such high proportions have not been found necessary in any of the actual separations. Nitric acid in high concentrations must be avoided because of its oxidizing action on the reagent.

In operation, the test solution, containing the equivalent of 20 ml. concentrated sulfuric acid and 0.2 g. titanic acid, is brought to a volume of 400 ml., and the beaker is placed in a bath of cracked ice. A recently filtered 4 per cent solution of cupferron is added, drop by drop, with constant stirring, in considerable excess. The titanium comes down as a canary-yellow, flocculent precipitate which coagulates almost immediately and may be filtered without the aid of suction. After careful washing with ice-cold dilute hydrochloric acid, the precipitate is dried in an oven and ignited at high temperature to produce titanium dioxide, which is weighed as such. The operation is carried out in the cold because the cupferron appears to decompose even below the temperature of boiling water, forming an oily material which solidifies to a resinous mass on cooling.[1]

Volumetric methods are generally employed if large numbers of samples are analyzed regularly, because of the simplicity and speed of the operation. Such analyses involve reduction of the titanium by suitable means, usually a special type of Jones reductor, followed by reoxidation with a standard oxidizing agent. Ferric solutions are usually employed, for with this reagent the iron, which so often accompanies titanium in the sample and is reduced along with it, is not reoxidized and thus causes no interference. The presence of other impurities often found in titanium ores, however, causes erroneous results, and of these vanadium is the worst offender. The end point is readily detected by aid of an alkali thiocyanate which is added directly to the main solution and which gives a strong, brown color in the presence of ferric ions.

An oversize Jones reductor which has proved satisfactory consists of a dispensing burette 2 inches in diameter and 21 inches long, connected through a glass stopcock to a delivery tube approximately 0.5 by 3.5 inches. A plug of glass wool is fitted in the bottom of the burette, and on top of this is placed a 7-inch column of 10-mesh and 20-mesh zinc (500 g. of each), and above this a 5-inch column, approximately 500 g. of sticks about 0.5 by 2.5 inches in size. Before

charging into the reductor vessel, the zinc is amalgamated by slowly pouring a solution of 22 g. mercuric chloride in 200 ml. concentrated hydrochloric acid onto 500 g. of the metal in granular or stick form, covered with water. After thorough mixing, the treated product is washed with hot water until free from chloride.

The delivery tube of the reductor vessel is led into a 1-liter flask through one opening of a three-hole rubber stopper. A second hole serves as an inlet for carbon dioxide or a nonoxidizing gas, and the third opening as outlet for the gas.

The standard oxidizing solution is prepared from ferric ammonium sulfate, 30 g. of the crystalline salt being dissolved in 300 ml. of water to which has been added 10 ml. of concentrated sulfuric acid. Potassium permanganate solution is then introduced, drop by drop, until a faint pink color persists, to insure oxidation of any ferrous iron, and the volume is brought to 1 liter. The solution is then standardized against potassium permanganate solution of known strength. Sodium oxalate, supplied by the U. S. Bureau of Standards, serves as a splendid primary standard. A 50-ml. portion of the ferric solution is made up to 100 ml. in 5 per cent sulfuric acid, passed through the reductor as used for titanium, and titrated with the potassium permanganate solution of predetermined strength. Each milliliter is equivalent to approximately 0.005 g. titanium dioxide, and may be adjusted to this exact value if desired. A saturated solution of ammonium thiocyanate is used as indicator.

Before each use, the reductor is drained to the top of the granular zinc, and 200 ml. of hot 5 per cent sulfuric acid is added. This solution is drained slowly, the zinc is washed in this manner several times with boiling water, and drained again to the top of the layer of granular zinc. The hot solution of the sample to be analyzed, containing not more than 0.25 g. titanium dioxide equivalent in 125 to 150 ml. of 10 to 15 per cent sulfuric acid, is washed into the reductor. It is covered with a watch glass and the carbon dioxide is turned on so that a slow stream flows through the reducing flask to prevent oxidation by the air. After 15 or 20 minutes, with the gas still flowing continuously, the reductor is drained slowly to the top of the column of granular zinc and boiling 5 per cent sulfuric acid is added in amount just sufficient to cover the layer of stick zinc. The reductor is again drained to the granular-stick contact and washed with boiling water in the same manner until the total volume is almost 1 liter. The receiving flask is removed, 7 ml. of the indicator solution is added, and the titanium is titrated rapidly with the standard ferric

ammonium sulfate solution to a faint brown color, which persists for several minutes.

In carrying out the titration, greater accuracy is obtained by adding nearly all the standard solution required before agitation, and then mixing with a gentle rotary motion until the final end point. When not in use, the reductor should be filled with water above the column of zinc and covered with a watch glass.

Titanium dioxide pigments in general, and similar manufactured products, may be dissolved directly in a hot mixture of sulfuric acid and an alkali metal or ammonium sulfate, although more refractory materials, such as ores, may require fusion with potassium bisulfate, sodium carbonate, or a similar compound. A 0.25 to 0.50 g. sample of the pigment is weighed into a 250 ml. beaker, and 20 to 30 ml. concentrated sulfuric acid and 10 g. of ammonium sulfate are added. The beaker is covered with a watch glass and the contents are carefully boiled over a flame until solution is effected. A slight residue of undissolved siliceous material may be disregarded. After cooling, the product is diluted with water to a volume of 125 ml. to 150 ml.; if a white precipitate forms, indicating barium sulfates, it is filtered off and washed with hot 5 per cent sulfuric acid and finally with hot water until free from titanium. The washings are added to the main solution and the combined product is brought to the desired concentration before being transferred to the reductor. Other composite pigments are treated in a similar manner, although it may not be necessary to remove the insoluble material.

Ores may require a fusion treatment to convert them to soluble form. To illustrate, 0.5 g. finely ground ilmenite is mixed with 10 g. potassium bisulfate and heated in a covered crucible at a red heat for 1 hour. The melt is cooled, dissolved in dilute (10 per cent) sulfuric acid, and adjusted to the concentration specified under the section on pigment analysis. The insoluble residue is usually small and need not be removed from the solution.

From the following chemical equations involved in the volumetric analysis of titanium, chemical equivalents may be calculated readily.

$$2Ti(SO_4)_2 + Zn \rightarrow Ti_2(SO_4)_3 + ZnSO_4.$$

$$2KMnO_4 + 5Ti_2(SO_4)_3 + 8H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 10Ti(SO_4)_2 + 8H_2O.$$

$$2KMnO_4 + 5Na_2C_2O_4 + 8H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 5Na_2SO_4 + 8H_2O + 10CO_2.$$

$$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 \rightarrow K_2SO_4 + 5Fe_2(SO_4)_3 + 2MnSO_4 + 8H_2O.$$

$$Ti_2(SO_4)_3 + Fe_2(SO_4)_3 \rightarrow 2Ti(SO_4)_2 + 2FeSO_4.$$
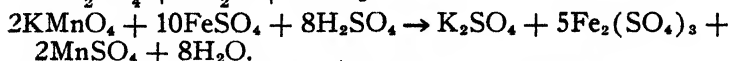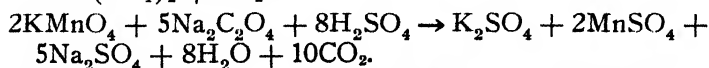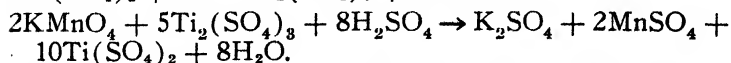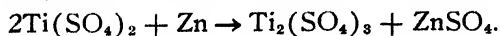
Titanium may be determined colorimetrically by comparing the intensity of the yellow color produced on adding hydrogen peroxide to a test solution with that of a solution of known titanium content similarly treated. This test is very delicate and 0.0003 g. titanic oxide in 100 ml. of solution gives a noticeable color under favorable conditions. Solutions deficient in acid, however, do not develop the maximum intensity of color, and it is necessary to have approximately 9.0 g. sulfuric acid in each 100 ml.

Methods of analysis given here are based on the assumption that no interfering elements are present. Detailed accounts of procedures for the separation of such elements are too numerous to be presented here.[2]

In the hydrolysis of sulfate solutions of ilmenite, the active or potential acid concentration is a critical factor and must be controlled carefully. It constitutes the sum of the free acid and the sulfate ions associated with the titanium, expressed as sulfuric acid, and represents the free sulfuric acid that will be present in the hydrolysis liquor after precipitation of the titanium as hydrous oxide. Sulfate combined with the iron, for example, is not released during the hydrolysis process, and for this reason is not included in this classification. The important active or potential acid concentration may be determined directly by titration with a standard alkali.[3] An accurately weighed sample of approximately 1.5 g. of the ilmenite solution is washed into a 400 ml. beaker containing 300 ml. of a 1 per cent solution of barium chloride and titrated, at room temperature, with a 0.25 normal sodium hydroxide solution employing methyl orange as indicator. The barium chloride serves the purpose of transforming the acidity from sulfuric to hydrochloric acid, which gives a sharper end point with the methyl orange. Just before the end point is reached, the barium sulfate coagulates and settles rapidly.

Chemical analysis alone cannot distinguish between blended and coalesced titanium dioxide-barium sulfate composite pigments; the two may be differentiated, however, by "dyeing" the pigment with methyl violet and examining it microscopically.[4] Mechanically mixed products show small violet particles of titanium dioxide and large white particles of barium sulfate, while the coalesced material exhibits gray particles of uniform size. Identification can also be established by appropriate fractionation by levigation. The various fractions from precipitated pigments have about the same composition, while blends give residues rich in the filler.

The presence of titanium dioxide in paint films may be readily detected colorimetrically by a reagent prepared by adding a few

crystals of potassium iodide, followed by an equal quantity of phenazone, to 1 ml. of 2 normal hydrochloric acid.[5] One drop of this reagent is placed on the paint film and allowed to remain for 1 hour. In the presence of titanium a deep golden-brown color develops.

Further information on the examination of titanium pigments may be obtained from "Standard Methods of Routine Analyses of Titanium Pigments," American Society for Testing Materials, Designation D186-37; American Standards Association, K43, 1937; American Society for Testing Materials, Standards, 1945, Supplement II, Nonmetallic Materials, Constructional; Federal Specification TT-P-141, Paints, Varnish, Lacquers, and Related Materials, General Specification (Method for Sampling and Testing); Federal Specification TT-T-425, Titanium Dioxide, Dry (Paint Pigment); Army-Navy-Aeronautical Specification AN-TT-T-436, Titanium Dioxide, Chalk Resisting, Dry (Pigment); and H. A. Gardner, "Physical and Chemical Examination of Paints, Varnishes, Lacquers, and Colors," Paint and Varnish Research Association, Washington, D. C.

Chapter 10

PRODUCTION OF SULFATE SOLUTIONS OF ILMENITE FOR PIGMENT MANUFACTURE

Introduction

Scientific literature contains the description of many methods for the production of titanium dioxide pigments, based for the most part on hydrolysis of sulfate, chloride, fluoride, nitrate, and chloroacetate solutions, but of these the sulfate processes are most important commercially. Nitrate solutions may be prepared by indirect means such as dissolution of orthotitanic acid, sodium titanate, or barium titanate in nitric acid, but these appear to be of little more than academic interest. Chloride and fluoride processes have been developed through the pilot plant stage and are reported to offer great promise both as to cost and quality of the pigment produced. Both hydrochloric and hydrofluoric acids are extremely corrosive, however, and special acid-resisting equipment must be employed. Since in large-scale operation this becomes quite a problem, plant design becomes complicated and expensive.

Hydrous titanium oxide of high purity may be satisfactorily precipitated by thermal hydrolysis from chloride and sulfate solutions containing large proportions of ferrous compounds as well as smaller amounts of other impurities; however, iron may be simply and effectively removed from the chlorides before this stage of the operation. Ferric chloride, the form in which the iron normally occurs, is practically insoluble in and immiscible with anhydrous titanium tetrachloride. It settles out on standing, so that separation may be effected by the simple expedient of filtration or decantation. Thus practically pure chloride solutions for hydrolysis may be obtained with little difficulty, but any iron compounds present should be reduced to the ferrous state, since in this condition it does not hydrolyze during the processing.

Fluorides of titanium, on the other hand, are quite stable, and, unlike the sulfates and chlorides, their solutions do not hydrolyze on boiling or dilution. The titanium is usually precipitated by adding an alkaline agent (ammonium hydroxide) after carefully purify-

ing the solution to remove the heavy metals which would also be thrown down as hydroxides and so injure the properties of the pigment. Since extremely small amounts of compounds of iron, vanadium, chromium, and manganese that are normally present in the ore would seriously injure the color and other properties of the calcined product, previous removal must be practically complete. This step may prove difficult. Serious corrosion and health problems would also be encountered.

A unique departure from the conventional processes based on the precipitation of titanium dioxide by the thermal hydrolysis of aqueous solutions, known as thermal splitting, is particularly applicable to chloride salts. By this process anhydrous titanium tetrachloride is converted directly to the dioxide with the liberation of elemental chlorine by heating the vapor in admixture with oxygen or air at high temperatures either indirectly or in a flame. This process has the advantage that chlorine rather than hydrochloric acid is recovered, but on the other hand the tetrachloride must be previously purified to a very high degree, since compounds of iron, vanadium, chromium, and other heavy metals normally picked up from the ore are precipitated with the titanium and seriously impair the color of the pigment.

Regardless of the type of solution employed, the fundamental steps include decomposition of the raw material (usually ilmenite ore) to obtain a soluble salt; dissolution of the reaction product; reduction of the iron component to the ferrous condition; clarification and filtration of the solution; adjustment of the absolute and relative concentration of the components, which may involve crystallization and vacuum concentration; precipitation of the titanium component, either as hydrous oxide by thermal hydrolysis after proper seeding or as hydroxide by adding an alkaline agent as with the fluoride; filtering and washing the product; treating the pulp with conditioning agents; calcination to convert the amorphous hydrous oxide to crystalline form having the desired pigmentary properties; and, finally, grinding, classifying, and pulverizing the calcined product.

A widely used commercial process for the production of titanium dioxide pigments is that developed by Blumenfeld, based upon the thermal hydrolysis of sulfate solutions prepared by dissolving ilmenite in sulfuric acid. The flow sheet of this method of manufacture is shown in Figure 6.

As originally employed, the process gave pigments of the anatase crystal modification. Other methods employ the same essential
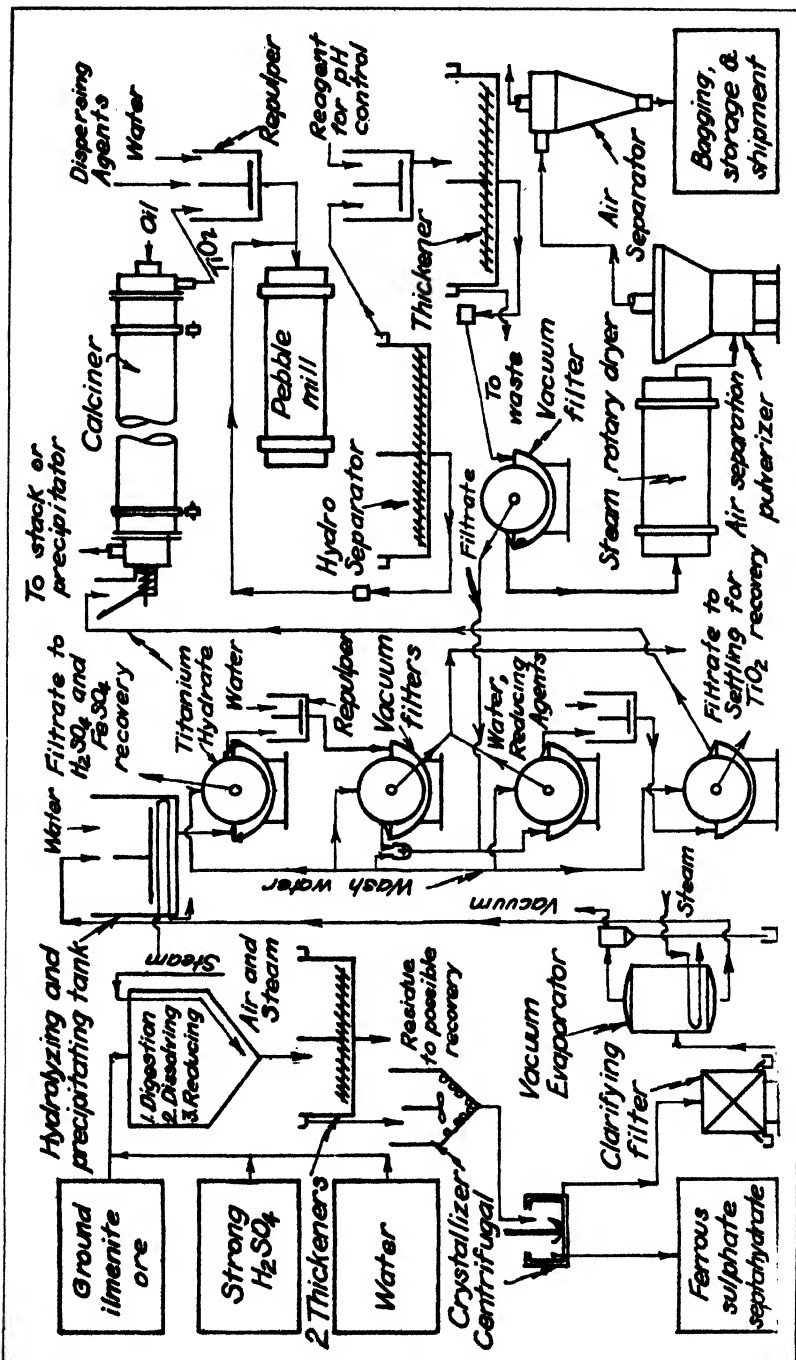
Figure 6. Flow sheet of the sulfate process for the manufacture of titanium dioxide pigments

steps, although the actual procedure of nucleating the solution and carrying out the hydrolysis may vary. Chloride processes employ chlorine for converting the titanium to the chloride, which may be dissolved in water and hydrolyzed in a manner very similar to that used with sulfate solutions, or the tetrachloride may be decomposed by thermal splitting to yield titanium dioxide and chlorine. The thermal splitting differs significantly in the earlier steps from the methods employing thermal hydrolysis of aqueous solutions. Coalesced composite pigments involve the same essential steps as those shown in the diagram.

Residues

The first processed titanium pigments were obtained as residues from ilmenite after leaching out a large part of the iron and other soluble constituents. Naturally, silica and other insoluble components, as well as some of the soluble compounds, remained with the titanium dioxide and exerted important and unfavorable influences on the properties of the final product, particularly on the color.

Farup [1] subjected ilmenite to an oxidizing roast at 500° C. to obtain an unsintered reddish-yellow product which disintegrated on addition to water and formed a fine suspension. Small quantities of electrolytes (sodium chloride) were then added to effect rapid coagulation and settling of the exceedingly fine-grained powder, which was then filtered and dried. The product was applicable for paint pigments and polishing powder.

In the next step forward, ilmenite was fused with an alkali metal compound; the melt so obtained was subjected to an oxidizing roasting process and heated with sulfuric acid to dissolve the soluble salts. [2] Sulfur dioxide was introduced to reduce the iron to the ferrous condition, and the suspension was then filtered and washed. The insoluble residue of crude titanic oxide was purified by repeated treatment with sulfuric acid, and the ferrous sulfate liquor was evaporated for recovery of sulfuric acid. Barton [3] heated ilmenite with sodium sulfide to ferrous sulfide and electrolyzed the product in aqueous sodium chloride so that the chlorine liberated effected decomposition and solution of the sulfides. The residue of relatively pure titanium dioxide was washed and dried for use. In a similar manner the ore was heated with sodium sulfide or a mixture of sodium sulfate and coal below the fusion temperature (625° to 825° C.) to form sodium ferrosulfide and sodium titanate. [4] The fritted product was then treated with dilute acid of such strength as to dissolve the iron compounds but not the titanium, and the

residue was washed and calcined. Instead of employing dilute hydrochloric acid, the iron could be extracted by passing sulfur dioxide into a water suspension of the fritted product.[5] By holding the melt of ferrosodium sulfide and sodium titanate in the fused state, a gravity separation into a titanium-rich upper layer and an iron-rich lower layer took place. After cooling, the titanate portion was separated mechanically and treated with dilute acid to remove the iron and other impurities, leaving relatively pure titanic oxide.[6] A residue of 90 to 99 per cent purity was obtained from the product of fusing ilmenite with such alkalies as sodium hydroxide or carbonate.[7] The melt was lixiviated to remove the excess alkali, and the residue was digested with hydrochloric acid of such concentration as to combine only with the iron and any remaining alkali. At this stage cold water was added to promote settling of the titanium oxide and to hold other compounds in solution.

Ilmenite was fused in a reducing medium with an alkali in such proportions as to form metatitanates.[8] The reduced iron was separated, and the slag was treated with an acid to dissolve the alkali oxide. A residue of titanium dioxide was obtained. Ilmenite suspended in a fused mixture of NaCl-FeCl$_3$ reacted above 550° C. with a preferential attack on the iron content.[9] The beneficiated titanium dioxide was recovered in the same particle size as that of the original ore. A mineral containing titanium, aluminum, and iron was ground to 100 mesh and converted to soluble compounds by fusing with ammonium sulfate under nonoxidizing conditions.[10] The solution was boiled to precipitate the titanium as hydrous oxide. Ammonia was recovered and reused. An artificial rutile[11] was obtained by heating titaniferous iron ores with coke in a proportion insufficient to reduce the iron completely, to form a fused mass which separated into a lower layer of molten iron and an upper slag layer consisting primarily of titanium dioxide. A mixture of titanite or sphene, with sodium chloride, was subjected at 900° to 1000° C. to superheated steam.[12] The melt was treated with a solution of hydrochloric acid obtained in the first stage, and the solid residue was used as a pigment or was converted to pure titanium dioxide in the conventional manner.

According to Von Bichowsky,[13] titanium dioxide free from iron may be prepared by subjecting ilmenite to a reducing roast, leaching the impurities as far as possible with dilute mineral acid, and heating the dried suboxide with sulfur or sodium sulfide under nonoxidizing conditions to convert the last trace of iron to the sulfide, in which form it may be extracted readily with hydrochloric acid.

The purified residue was then heated in air to convert it to titanic oxide of pigment grade.

Jebsen [14] crushed the melt obtained on fusing titaniferous ores with alkaline agents and subjected it to an oxidizing roasting process. This product was heated with sulfuric acid, and sulfur dioxide was introduced into the solution to reduce the iron to the ferrous condition. The resulting ferrous sulfate liquor containing a small amount of titanium sulfate was employed in a subsequent roast. By repeated acid treatments the ferrous sulfate was extracted, leaving pure titanic acid. According to a later development, solution of the reaction product obtained by heating ilmenite or other titaniferous ore with sulfuric acid was carried out in the presence of a sulfurous reducing agent such as pyrite, which was added before or during the reaction. [15]

In a method developed by Booge [16] for producing a practically iron-free titanium dioxide concentrate, ilmenite or similar ore was heated in air at 500° to 1000° C. and the resulting oxidized product was subjected to the action of gaseous hydrochloric acid at 600° to 800° C. to convert the iron to ferric chloride. This compound, which was volatile, distilled off at the temperature employed. Crude hydrous titanium oxide containing iron and other foreign substances was first treated with strong sulfuric acid or a bisulfate at an elevated temperature, and the reacted mass was disintegrated and ground with sodium chloride. [17] This mixture was heated at 300° to 500° C. with periodic stirring to produce a porous sintered mass which was cooled and leached according to the counter-current principle. The residue of purified titanic oxide was then filtered, washed, and dried. Any titanium salts in the filtrate were precipitated hydrolytically by boiling, then added to the main product.

By carbon reduction of Wyoming titaniferous iron ores, followed by acid leaching, residues containing 2.1 to 2.8 times the titanium dioxide content of the original ore were obtained. [18] Reduction in the presence of sodium carbonate, followed by wet magnetic separation, gave a magnetic fraction containing 90 to 95 per cent iron and a nonmagnetic fraction containing 40 to 70 per cent titanium dioxide. Ravenstad and Moklebust [19] heated ilmenite or titanomagnetite with a reducing gas at 700° to 900° C., or with carbon at 1000° C., in a rotary furnace to obtain metallic iron in a finely divided form which was reoxidized by air and steam in the presence of carbon dioxide at 50° to 100° C. The iron oxides were removed by magnetic or electroflotation methods, leaving a concentrate containing 68 per cent titanium dioxide. [20] Brassert

produced titanium-free steel and a highly concentrated titanium slag from ores containing ilmenite. The magnetic iron oxide was selectively reduced to sponge iron, and the product was heated in a melting furnace with lime to form a slag with the titanium oxide and gangue of the ore. Carbon was then added to the bath to reduce sufficient iron oxide of the ilmenite in order to effect a concentration of titanium in the slag.

Enriched iron ores containing titanium, vanadium, and chromium were heated with charcoal at 500° to 800° C. in the presence of a sodium compound to reduce the magnetite to sponge iron and convert the chromium and vanadium compounds to the corresponding sodium chromate and vanadate.[21] Ilmenite remained unchanged. The vanadates and chromates were dissolved and the iron was removed by magnetic separation. In a process developed by Campbell,[22] titaniferous magnetite was crushed and screened; fines were sintered with sodium carbonate, and the coarse ore and sinter were smelted in a blast furnace. The pig iron containing most of the vanadium was converted to steel in a Bessemer converter. The slag was ground and leached with sulfuric acid, and titanium dioxide was precipitated from the purified solution by thermal hydrolysis and processed in the usual manner to produce pigment. Recovery of titanium was 80 per cent. The sodium carbonate was recovered and reused.

Fusion of Ores

The initial products obtained as residues from ilmenite were fairly pure titanium dioxide with relatively high tinting strengths, but were quite yellow, were expensive to manufacture, and fell far short of the original conception of a high-grade white pigment.

The next improvements were processes in which the titanium content of the raw material (ilmenite) was converted to soluble form, dissolved, and reprecipitated from the dilute solution after removal of suspended solids. This allowed a more complete separation of iron, silica, and other undesirables, and thus gave titanium dioxide of higher purity and improved pigment properties, particularly color. The available ores of titanium are quite refractory. In the pioneer period, fusion with sodium hydroxide, sodium hydrogen sulfate, potassium carbonate, sodium sulfide, and similar reagents was resorted to, and the resulting melts were dissolved in dilute acids to obtain the desired solution.

In an early process, ores of titanium were fused with alkali metal sulfides [23] and the melt was boiled with dilute sulfuric acid

of such strength as to dissolve only the iron. The residue was
washed and heated with stronger sulfuric acid to form titanium
sulfate, which was dissolved in water. Any iron present was re-
duced to the ferrous condition, and the solution was clarified and
boiled to precipitate the titanium as hydrous oxide. To break down
rutile or other difficultly soluble titanium ore, Ryan and Knoff [24]
fused the finely divided material with an alkali metal compound
such as potassium carbonate or sodium acid sulfate in proportions
sufficient to convert the titanium to acid-soluble form, i.e., about
5 parts of titanium oxide to 1 of sodium oxide. The crude product
was digested with 93 per cent sulfuric acid at 200° to 220° C. until
the titanium was converted into soluble sulfates. Rossi [25] fused
rutile and ilmenite with sodium acid sulfate and dissolved the melt
in boiling water. By a similar method [26] the ore was heated with
a mixture of sodium bisulfate and sulfuric acid below the fusion
point (120° to 300° C.) until a solid cake was obtained. The cooled
mass was crushed and dissolved in water. Iron may be removed in
a preliminary stage by heating the ore with carbon at 900° to
1050° C. and leaching the spongy metal with ferric chloride.

Barton and Kinzie [27] heated an intimate mixture of ore, alkali
metal sulfate, and sulfuric acid at 200° to 350° C. (below the fusing
point) to form water-soluble sulfates. Readily soluble titanium
compounds [28] were prepared by heating ilmenite with sulfuric acid
in a solution of potassium sulfate. According to another modifica-
tion, finely ground rutile was heated with sodium hydroxide at
280° to 650° C. without fusion, and the product was leached with
water and dilute sulfuric acid. The residue of crude titanium
dioxide was redissolved in strong sulfuric acid and reprecipitated
to improve its purity.[29] A product consisting of calcium titanate
and magnetite was obtained by roasting titaniferous iron ore [30]
with calcium oxide in equimolecular amounts, and the iron was
removed by magnetic separation. By an alternate method, the iron
oxides were reduced to the metal and separated magnetically as
before. Lubowsky [31] calcined finely ground rutile with magnesium
oxide at a temperature of 1400° to 1500° C. to form magnesium
titanate. This was cooled, ground, and heated at 90° C. with
concentrated sulfuric acid to form soluble sulfates. The slurry was
diluted with water and cooled to 0° C. to effect separation of
magnesium sulfate by crystallization.

On roasting finely ground ilmenite with a mixture of calcium
oxide and sodium carbonate at 900° C., a mixture of calcium titanate
and sodium ferrate was formed.[32] The soda was extracted from

the product by leaching with water, and over 95 per cent of the iron dissolved in 10 per cent sulfuric acid. The residue of calcium titanate was heated at 165° C. with concentrated sulfuric acid to produce calcium sulfate and soluble titanium sulfate. On fusing crude titaniferous material containing alumina and silica with lead monoxide, a mixture of titanates and silicates resulted from which the aluminum oxide crystallized on cooling.[33]

Reduction and Leaching of Ores

In a combined fusion and reduction process,[34] a mixture of ilmenite, sodium carbonate, and anthracite coal dust was heated at 800° C. in a roasting furnace. The product was discharged in water, and the solution was carbonated to effect separation of the sodium carbonate. After extracting the iron with dilute sulfuric acid, the residue was filtered, dried, and heated at 150° to 180° C. with strong sulfuric acid to convert the titanium to soluble salts. The temperature was then raised to 200° to 225° C., and the sulfur dioxide liberated by the reaction between sulfuric acid and carbon reduced the titanium to the trivalent state. In a similar process developed by the same workers, the ore was heated with sodium carbonate, a reducing agent (coke), and a flux at 1000° C. The product was then washed with water and treated with sulfuric acid to form titanium sulfate.[35] Raffin [36] heated ilmenite with sodium carbonate and coal to reduce the iron to the metal, and, after leaching it with dilute sulfuric acid, treated the residue with stronger acid to form soluble titanium sulfate. In the presence of an alkali chloride, total reduction of the iron oxides was effected at 700° to 800° C.[37] By fusing titanium ore with barium carbonate and coal, a slag composed essentially of barium and titanium oxides and metallic iron was formed. After removing the iron by magnetic separation, the product was mixed with sulfuric acid and heated to form titanium sulfate and barium sulfate.[38] Similarly, ilmenite or titaniferous iron ore was heated with barium sulfate and coke (a small amount of sodium sulfate could be included in the charge), and the product was leached with water to dissolve barium hydroxide and barium sulfide. The residue was then separated and treated with dilute acid to dissolve the iron sulfide, and the crude titanium dioxide remaining was treated with concentrated sulfuric acid to convert it to soluble form.[39]

Buckman [40] heated a mixture of ilmenite, sulfur, barium sulfate, and coke in a blast furnace and dissolved the melt in strong hydro-

chloric acid. A product composed primarily of sodium titanate and metallic iron, obtained by smelting titaniferous iron ore with coke and sodium hydroxide, was lixiviated with hot water and treated with 50 to 60 per cent sulfuric acid to convert the titanium content to soluble form.[41] A similar method applicable to sphene has been described by Tatarskii.[42] One part of the finely ground concentrate was mixed with 4 parts of sodium sulfite and 0.8 part powdered coke and heated for 1 hour at 850° C. The cooled melt was digested with water, and the residue was washed with sulfurous acid solution and calcined at 800° to 850° C. This crude titanium dioxide product was fused with potassium acid sulfate (1 to 12) at 430° C. for 5 hours and poured into water to obtain a solution of titanium sulfate. Yamamoto[43] fused a mixture of titanium ore, an acid sulfate, and carbon, and extracted the melt with water. By treating the product with dilute mineral acid and sulfur dioxide, a titanate was obtained as residue.

By another approach Bachman[44] heated ground ilmenite with an excess of coking coal in a retort to obtain a product consisting primarily of metallic iron, titanium oxide, and carbon. After leaching the iron with dilute sulfuric acid, the residue was treated with concentrated sulfuric acid to yield a solution of titanic and titanous sulfates. In a similar process,[45] ilmenite or titaniferous iron ore was subjected to a reducing roast at 900° C. The product was lixiviated with dilute acid to remove the sponge iron, and the titaniferous residue was then heated with concentrated sulfuric acid and sodium bisulfate. Whittemore[46] heated titaniferous iron ore at 950° C. with 25 to 33 per cent carbon and dissolved the resulting sponge iron in dilute acid. The residue, as before, was separated and heated with concentrated sulfuric acid to form soluble titanium sulfate. Magnetic concentrates from titaniferous iron ores were heated with coke, oil, or tar at 900° to 1100° C. to reduce the iron component to the metallic state, and this was then dissolved from the friable product with dilute hydrochloric or sulfuric acid.[47] The titanium residue was dried for use or dissolved in strong sulfuric acid. In a modified process, the ilmenite was reduced with coal at 1000° to 1100° C., and the sponge iron was leached with ferric chloride solution.[48] Mixtures of 2 parts concentrate (44.7 per cent titanium dioxide and 37.7 per cent iron), and 1 part brown coal at temperatures above 1000° C. gave best results. By treating the reduced product at room temperature with 15 parts of solution containing 20 per cent ferric chloride and 3 per cent hydrochloric acid, 98 per cent of the iron was removed. Moore[49] heated finely

crushed hematitic ilmenite with 34 per cent pulverized charcoal in a covered crucible for 7 hours at 900° to 1000° C. to produce a product containing 24.6 per cent titanium dioxide and 55.2 per cent iron of which 50.4 per cent was in the metallic state and 11.1 per cent carbon. Magnetic concentration was unsatisfactory, so leaching with ferric chloride was employed. Carbon was removed by ignition. Farup[50] heated ilmenite with a carbonaceous reducing agent at a temperature high enough to reduce the iron component to the metallic state but below that required to reduce the titanium compounds, and heated the product with concentrated sulfuric acid of such strength as to dissolve the titanium compounds without attacking the iron. According to Fitzgerald and Bennie,[51] the iron oxides of ilmenite were completely reduced to metallic iron by heating the ore at 1000° C. with 7.3 to 10.6 per cent carbon. The sintered mass was crushed and the iron was removed by magnetic separation, followed by treatment with 10 per cent sulfuric acid. A sponge product made by reducing ilmenite ore with charcoal gave a yield of metallic iron of 79.5 per cent, and leaching with ferric chloride solution extracted 96 per cent of the iron, leaving a concentrate containing 53.6 per cent titanium dioxide.[52] Small quantities of copper, nickel, lead, and cobalt were separated in concentrated form. Electrodeposition of the iron gave a product 99.96 per cent pure with a current efficiency of 94.3 per cent.

Titanium dioxide may be separated from ores (ilmenite) by concomitant reduction and oxidizing volatilization.[53] An air blast heated at 750° to 850° C. was passed over thin layers of a mixture of powdered ore and reducing fuel which were moved forward by air jets. Bancroft[54] subjected titaniferous iron ores to a reducing roast in the presence of fluorspar to produce metallic iron without reducing the titanium dioxide. Von Bichowsky[55] reduced the titanium content of ilmenite to an amorphous suboxide by heating the ore with carbonaceous material, leached out the impurities (iron) with dilute hydrochloric acid, and heated the residual suboxide of titanium with sodium sulfate under reducing conditions so as to convert any remaining iron compounds to sulfides. The latter were leached out with hydrochloric acid and the purified residue was oxidized to titanium dioxide of pigment grade.

In a related process, ilmenite was heated with coal until the titanium was reduced to the trivalent state.[56] The product was treated with sulfuric acid in such proportions as to form a solution of titanium sulfate, and this was diluted and boiled to precipitate basic titanium sulfate. By heating a mixture of titania and zircon

with carbon under reducing conditions at 900° to 1000° C. without sintering, and cooling in a nonoxidizing atmosphere, dititanosotitanic carboxide [57] was formed, leaving the zircon unattacked. This carboxide may be used in preparing other compounds of titanium. A method has been described by which the ferric oxide of oxidized ilmenite was reduced with hydrogen at high temperatures.[58] The iron was separated, leaving a high-grade titanium dioxide concentrate which was used in pigment making.

Iwase [59] developed a novel process of separating titanium dioxide directly from titaniferous iron ores, which involved reduction with carbon. To this sponge-iron-containing product were added as fluxes from 25 to 40 parts of calcium oxide and 35 to 55 parts of manganese oxide for each 100 parts of titanium dioxide, and the mixture was then smelted. The silica content of the charge was so regulated that the slag which was produced consisted of an eutectic mixture of titanite and pyrophanite, with a resulting content of titanium dioxide higher than 35 per cent and of manganese oxide higher than 15 per cent, and having a correspondingly low melting point. By reducing titaniferous magnetite with solid carbon, with reducing gases, or with a mixture of the two at 900° to 1000° C., and then smelting the residue, pure iron as one product and a slag rich in titanium, vanadium, and chromium were obtained.[60]

Selective Solution of Components of Ores

To dissolve selectively the iron content, ilmenite or a similar ore was heated with 40 per cent sulfuric acid at 170° to 180° C. for 6 hours in the presence of a reducing agent such as tervalent titanium compounds, copper and sulfur dioxide.[61] Carbon and cupric iodide were found to catalyze the reaction. After most of the iron had been extracted, the residue was dissolved by heating with stronger sulfuric acid, and the solution was hydrolyzed to produce iron-free titanium dioxide.

Farup [62] effected a selective solution of the iron content of ilmenite by heating the pulverized ore with three times its weight of 20 per cent hydrochloric acid at 70° to 80° C. for 12 hours. The titanium dioxide residue was then converted to soluble form by digestion with concentrated sulfuric acid. In an improved process [63] the finely ground ilmenite was leached with hydrochloric acid of specific gravity 1.5 for 2 or 3 days at 50° to 60° C., after which the temperature was raised to 85° to 95° C. to precipitate any dis-

solved titanium, leaving a solution of ferric and ferrous chlorides. The crude titanium dioxide residue was purified by dissolution in strong sulfuric acid and reprecipitation. Hydrochloric acid effected almost quantitative extraction of iron from titaniferous magnetites.[64] On heating a mixture of 100 g. of the finely divided ore and 100 ml. of 20 per cent hydrochloric acid at the boiling temperature with agitation, 97.3 per cent of the iron was extracted in 6 hours and 98.2 per cent in 24 hours. The efficiency of the process increased with fineness of milling of the titanomagnetite concentrate. By a modified method,[65] ilmenite was mixed with coal and heated at 500° to 800° C. to reduce all ferric iron to the ferrous form but not to the metallic state so that the ore was not appreciably changed physically. The ferrous compounds were then dissolved selectively in dilute acids leaving a residue of crude titanic oxide. According to Yuravskii,[66] the intensity of attack of titanomagnetites by hydrochloric acid decreased with the content of iron and finally became negligible. Dunn [67] extracted phosphorus and other impurities from ilmenite of the Virginia and Norway type, to be used in the manufacture of pigment, by heating the unground ore with 5 to 10 per cent sulfuric acid at 82° to 93° C. Such treatment did not dissolve the titanium content of the ore. According to an interesting procedure, a mixture of ilmenite and pyrite was subjected to the action of moisture and air to effect a preliminary oxidation of the sulfides, and the product was heated with added sulfuric or hydrochloric acid to dissolve selectively the iron content.[68] Sulfur dioxide was employed by Stahl [69] to extract titanium from ores and slimes.

Iron and other impurities were separated from titaniferous material by electrolyzing an alkaline solution or suspension (for example, a suspension of ilmenite) at 90° to 120° C. under a pressure of hydrogen or air of 20 atmospheres, employing an insoluble anode of carbon, nickel, or chromium steel.[70] The iron was deposited in a metallic state.

Direct Reaction with Sulfuric Acid

The fusion, reduction, and combination processes were slow,. cumbersome, and expensive of operation, but fortunately later investigations revealed that the titanium content of ilmenite, the most available ore, can be converted economically to water-soluble form by heating the finely ground material directly with strong sulfuric acid.

Weintraub [71] found that finely divided ilmenite can be decomposed quantitatively with concentrated sulfuric acid in a proportion equal to that theoretically required to give normal salts of the base constituents of the ore. Pulverized ore was mixed with approximately 2 parts by weight of 93 per cent sulfuric acid and heated in a cast-iron vessel. At 100° C. the exothermic reaction started and the ilmenite was converted into a solid mass composed largely of soluble titanium and iron sulfates. Farup [72] mixed finely ground ilmenite with a relatively large proportion of concentrated sulfuric acid (60° Bé), and heated the slurry gently to start the reaction which proceeded vigorously with a great evolution of heat. The grayish solid mass obtained was then roasted at 900° C. to decompose the sulfates and distill off the sulfuric acid, and the product was ground to a yellowish pigment. A later development involved the separation of most of the iron from the reaction product. [73] Finely divided ilmenite was mixed with one or two parts of concentrated sulfuric acid and heated gently to initiate the reaction, which then proceeded vigorously with evolution of much heat. The solid sulfate mass obtained was then heated in air at about 600° C., and at this temperature sulfates of titanium were converted to insoluble oxides while the ferrous sulfate remained unchanged. The cooled mass was then leached with water, whereby practically all the iron was dissolved, leaving the titanium oxide together with the gangue. This crude product was further refined by heating with sodium chloride at 700° C. and extracting the impurities from the mass with water.

Rossi and Barton [74] digested ilmenite with 95 per cent sulfuric acid, in a proportion by weight of 2.5 to 2.6 times the titanium dioxide content, to obtain a soluble product that was leached in about three times its volume of water. Blumenfeld [75] found that titanium-bearing ores (ilmenite) were decomposed by heating with 70 to 90 per cent sulfuric acid at 130° C., and finally to 220° C. The reaction product was dissolved in water in such proportions that the final solution contained 15 per cent titanium dioxide. In a similar procedure [76] the ore was decomposed as before by heating with one or two parts by weight of 80 per cent sulfuric acid, and the reaction product was treated with three parts of water or less. A soluble product was obtained by heating ilmenite with 70 to 90 per cent sulfuric acid at 150° to 180° C. for 1.5 hours or for some time after the mass had assumed the form of a dry powder. After cooling to 50° C., a limited quantity of water was added in small portions to dissolve practically all the titanium sulfate and only

15 to 20 per cent of the iron sulfate. Sponge iron was introduced to reduce any ferric salts to the ferrous state. After separating the solution, the iron sulfate left in the residue was leached out and treated to recover sulfuric acid.[77] Similarly, finely ground ilmenite was heated with 96 per cent sulfuric acid at 160° C. until the reaction was complete.[78] The product was agitated with a limited amount of water to dissolve the titanium component together with some ferrous and ferric compounds. Finely divided metallic iron was introduced to convert the latter component to the ferrous state. After filtration, the ferrous sulfate was largely removed by crystallization.

A further improvement[79] was the production of a solution of titanyl sulfate, which gave titanium dioxide of the same chemical and physical properties as the normal sulfate solution. Finely ground ilmenite was mixed with concentrated sulfuric acid so that on the 100 per cent basis the ratio of acid to titanium dioxide was 1.2 to 1.8. The mixture was gradually heated to 120° C. to initiate the reaction, and the paste obtained was further heated to 140° to 250° C. to produce a solid product. The temperature, however, was held below the constantly increasing boiling point. A solution containing 150 to 250 g. per liter titanium dioxide was obtained by leaching the reaction cake.

Jebsen[80] mixed pulverized ilmenite with 94 per cent sulfuric acid in amount less than that required to form normal sulfates of the base-forming elements present and obtained a slimy product which on heating to 100° C. reacted vigorously, yielding a more or less solid cake. A ratio of acid to ore of 1.44, instead of the theoretical 1.9 required to decompose the particular sample of ilmenite and transform its constituents into normal sulfates, gave good results. The solution of titanium and iron sulfates obtained by leaching the cooled product on the counter-current principle was treated with metallic iron to reduce the ferric compounds to the ferrous condition. In preparing such a water-soluble compound by the thermal reaction between finely divided titaniferous material and concentrated sulfuric acid, Schmidt[81] employed proportions so as to get a solid reaction mass on heating, and added 0.5 to 10 per cent (based on titanium dioxide) of a crystalline seeding agent such as hydrated or anhydrous titanyl sulfate or the products of a previous operation. Ilmenite or artificially prepared hydrous or dehydrated titanium oxide served as the starting material. If the more refractory rutile ore was used, it was first used with an alkali to form the corresponding titanate. For example a mixture of 1000 parts of pulverized rutile and 1250

parts of a 20 per cent solution of sodium carbonate was evaporated to dryness and roasted at 950° C. to obtain sodium titanate. On heating 600 parts of this material with 1140 parts of concentrated sulfuric acid and seeding the product with crystalline titanyl sulfate, a crystalline, porous, readily soluble mass was obtained. By another approach, pulverized ilmenite was impregnated with sulfuric acid and heated to 300° C. in such a manner as not to introduce water.[82] The concentration and proportion of acid was such as to react with the titanium and other bases to give a semidry product. The ore in pulverized form may also be decomposed with sulfuric acid in steps.[83] In this process the ilmenite is first heated with less acid than that required for reacting with all the titanium, the product is lixiviated, and the insoluble residue is again treated with another portion of acid. The hydrous titanium oxide obtained from the solution by thermal hydrolysis is further purified by treating it in the same manner as the original material.

ᴗ The product obtained by reacting finely ground ilmenite concentrate with twice its weight of sulfuric acid (specific gravity 1.72) at 140° C. was leached with water at 97° C. for 8 hours to obtain a solution of titanium and iron sulfate.[84] After reducing any ferric ions by introducing metallic iron or by electrolysis, the solution was cooled to crystallize the ferrous sulfate. According to the method of Monk and Ross,[85] titanium-bearing ores (ilmenite) were agitated with a small proportion of sulfuric acid of specific gravity 1.55 and heated to about 175° C. until the mass thickened. More acid was added, either continuously or intermittently as the reaction proceeded, to convert the titanium to the normal sulfate. . The initial addition of acid may be sufficient to form ferrous sulfate and titanyl sulfate. Wrigley and Spence [86] heated a mixture of ilmenite and sulfuric acid to the reaction temperature by injecting steam directly into the mass. By this method the strength of the acid may be regulated. The solution of iron and titanium sulfates obtained by extracting the digestion cake with water was treated with metallic iron to convert all ferric salts to the ferrous condition and hydrated ferrous sulfate was separated by crystallization on cooling. A proportion of other acids, e.g., hydrochloric and oxalic, may be added to the solution at this stage. Kingsbury and Grave [87] added phosphoric acid or soluble phosphates to the normal ilmenite-sulfuric acid mixture in such a proportion that the content of this agent expressed as phosphorus pentoxide was 0.1 to 2 per cent of the weight of the ore. This produced a better dispersion of the finely ground ilmenite in the acid so that on initiating the reaction by

the conventional methods a higher recovery of titanium was obtained.

Kramer [88] treated titanium containing residues such as mud or slime from clarification underflow with strong sulfuric acid (oleum) in amount considerably in excess of that theoretically required to produce normal sulfates of the titanium and other metallic constituents, and utilized the resulting mixture in acid attack of a fresh charge of ore. In general such mixtures were employed as would yield an acid concentration of approximately 96 per cent at a temperature of 150° C. or above, whereby the acid-titanium dioxide ratio obtained was many times that normally employed in attacking ilmenite. Yields of titanium of 96 to 98 per cent were obtained. In an example, 315 pounds of mud suspension containing 300 to 500 g. per liter solid was placed in a pan, and 2000 pounds of oleum was added with agitation. The mixture became quite hot and reaction took place. Acid strength was adjusted by adding recovered hydrolysis liquor containing 25 per cent sulfuric acid, and the temperature was raised to 215° C. by the introduction of steam, during which time almost complete conversion to soluble sulfate of the titanium dioxide present in the mud was accomplished. This liquor was used for diluting ilmenite-oleum mixtures to set off the reaction or in dissolving the reaction cake. Alternatively, the mud-acid reaction product was mixed with cold acid and ground ilmenite, and the reaction was set off by injection of steam or addition of water to raise the temperature. Mud was mixed with strong acid, above 85 per cent, and the mixture was added to an attack vessel with a suspension of ilmenite and cold acid. The reaction was initiated by conventional methods. The insoluble portion of the reaction product of ilmenite and sulfuric acid left after leaching out the soluble sulfate was concentrated by a mechanical flotation process and the concentrate of unattacked ore was again treated with sulfuric acid. [89] Moran [90] mixed such residues with dilute sulfuric acid from a previous hydrolysis reaction to form a free-flowing slurry, and added this product to a regular digestion mixture. To get more complete reaction [91] the residue was dried and heated with hydrogen or illuminating gas at 800° to 1300° C. to reduce the iron to the ferrous state. The reduced product was mixed with regular ilmenite ore and treated with concentrated sulfuric acid in the usual manner. Bousquet and Brooks [92] heated the residue with an excess sulfuric acid at 200° to 300° C. to effect reaction, and further heated the solid product at the same temperature to expel the excess acid.

Shtandel [93] treated titaniferous magnetite containing 39.1 per cent titanium dioxide and 49.4 per cent iron with sulfuric acid solution of 10 to 60 per cent concentration at various temperatures up to the boiling point. In all the experiments the ratio of acid to ore was 1.5 times the theoretical. The highest extraction, 38.6 per cent titanium dioxide and 45.5 per cent iron based on the original ore, was obtained with 60 per cent acid at the boiling point. On refluxing ilmenite or blast furnace slag from titaniferous iron ores with 40 to 60 per cent sulfuric acid for 6 to 8 hours, 90 to 95 per cent of the titanium was dissolved. By employing stronger acid, however, a water-soluble precipitate containing much titanium was obtained. [94] Under optimum conditions, 83 per cent of the titanium dioxide content of such slag was extracted with sulfuric acid of specific gravity 1.84 in 2.5 hours. [95] The sample was ground to 200 to 250 mesh and heated with 1.7 parts by weight of the acid to 180° to 200° C. From a study of the reaction between ilmenite from Korea and strong sulfuric acid, Matsubara [96] concluded that the ore must be finely ground and that too much excess acid reduces the recovery of titanium dioxide in the later hydrolysis step.

A mixture of soluble sulfates of titanium and iron was obtained by gradually adding oleum to damp pulverized ilmenite with constant stirring. [97] The reaction product was dissolved in water and diluted to obtain a solution of the desired concentration.

According to Grachev, [98] the titanium and iron components of titanomagnetite concentrates were dissolved in 40 to 50 per cent sulfuric acid two to three times faster if the iron was kept reduced electrolytically to the ferrous condition as dissolved. Recovery of titanium of 70 to 100 per cent was obtained at 94° to 97° C. in the presence of 10 to 25 per cent excess acid.

Porous Digestion Product

The next steps forward were methods of carrying out the reaction between finely divided ilmenite and strong sulfuric acid to produce a porous, water-permeable, solid product which could be dissolved readily in the reaction tank without the necessity of first digging out and breaking up the cake. Several procedures have been described, but in general this effect is obtained by blowing air through the reacting mass as it solidifies.

Washburn [99] reacted finely ground ilmenite with concentrated sulfuric acid (72 to 92 per cent), under such conditions as to produce a porous, water-permeable solid to facilitate its subsequent solu-

tion. The acid-ore mixture was heated by blowing in hot air or live steam from 80° to 120° C., at which temperature a small amount of water was added to initiate the reaction. A local dilution of the acid took place, producing a localized overheating. At this region the exothermic reaction immediately commenced and energetically propagated throughout the mass with copious evolution of sulfur trioxide fumes. As a rule one injection of water was enough, although more injections were necessary in some cases. During the reaction the mass was kept in an agitated condition by injection of air or other gas to obtain the porous liquid-permeable product. The air stream was continued until the mass solidified to ensure a highly uniform and cellular cake. Instead of heating the mixture in the reaction vessel, the components may be preheated before bringing together. The reaction, which is exothermic, usually liberates enough heat to carry it to completion. With certain ores, notably Norwegian ilmenite, the mixing and stirring of the finely ground material with sulfuric acid may cause the reaction to take place without preliminary heating. In any case the reaction may be controlled by adjusting the volume, temperature, and period of application of the gas. The porous cake is dissolved in the reaction vessel without further treatment.

' In an example, 10 tons of pulverized ilmenite was mixed in a cylindrical, conical-bottom tank with 10 to 24 tons of sulfuric acid (72 to 92 per cent), and steam was injected into the mixture through a nozzle at the bottom until the temperature reached 80° to 120° C., usually 100° C. The mass thickened, and at this stage from 2 to 12 quarts of water was introduced through a pipe at the bottom of the vessel to initiate the reaction which rapidly spread throughout the mass. During the reaction, and while the product was solidifying, a vigorous stream of air was injected through a nozzle at the bottom of the tank. After the mass had solidified and cooled to the desired temperature, the air supply was shut off and water or dilute sulfuric acid was introduced from the bottom through the nozzle formerly used for air. To the resulting solution, consisting of a mixture of titanium and iron sulfates, scrap iron was introduced in a lead basket to reduce all the ferric component to ferrous, and a small proportion of titanic sulfate to titanous condition. The residue, consisting essentially of unreacted ore and silica, became suspended in the solution during the process. ·

According to Cauwenberg,[100] a porous cake may be obtained by adding a small proportion of a carbohydrate or other carbonizable material to the ilmenite-sulfuric-acid mixture before initiating the

reaction. The normal reaction is exothermic, and the large amount of steam and other gases liberated within the mass tends to make it porous. The degree of porosity attained, however, depends upon the viscosity of the mass, which in turn determines the extent to which the evolved steam is retained as the product solidifies. Optimum viscosity may be developed by adding the proper proportion of the organic material.

To illustrate, ilmenite ground to 200 mesh was mixed with twice its weight of 66° Bé sulfuric acid and the suspension was heated rapidly to a temperature of 120° to 130° C., and 0.6 per cent dextrin in dry form, based on the ore, was added. The reaction between sulfuric acid and dextrin resulted in a voluminous production of finely divided carbon which greatly increased the viscosity of the mass, and the heat liberated initiated the reaction between the ore and the acid, which then proceeded without external application of heat. Steam was rapidly evolved within the mass, and with the increased viscosity a large proportion of it was retained so that a liquid-permeable, solid cake resulted. This porous reaction product was more readily dissolved in water to yield a solution of titanium and iron sulfates.[101] To attain this end, Coffelt first heated ilmenite with sulfuric acid of 76 per cent strength to obtain a semiliquid mixture. A further quantity of acid of at least 95 per cent strength was then added, and the reaction was completed at an elevated temperature to produce a porous solid cake.

Pressure Digestion

Buckman[102] treated titanium ores such as ilmenite and rutile, which had been pulverized and preferably air floated, with sulfuric acid at high temperatures and pressures to obtain water-soluble products. Pressures up to 200 pounds per square inch were employed. After the reaction had gone to completion, water was added to dissolve the titanium and iron sulfates formed. According to a later process, finely ground ilmenite was heated under pressure at 180° C. with 20 to 40 per cent sulfuric acid to form a solid mass which was leached with water containing enough trivalent titanium to reduce the ferric iron to the ferrous state.[103]

Titanium ores containing iron in the ferric state, such as arizonite,[104] were subjected at 550° to 650° C. to the controlled action of a reducing gas to convert the ferric compound to the ferrous condition without the formation of metallic iron. The treated ore was then digested with sulfuric acid under pressures corresponding

to temperatures of 135° to 180° C. to form soluble salts of the titanium, iron, and other basic constituents.

Continuous Processes of Digestion

A continuous process for decomposing titanium ores with sulfuric acid was developed by Booge, Krchma, and McKinney.[105] Previous intermittent methods present inherent difficulties, so that such digestions are usually carried out in relatively small or extremely large batches. In the latter case large cylindrical tanks with cone-shaped bottoms are used, and the charge is agitated by injection of steam or air. Ilmenite can be mixed with sulfuric acid of different concentrations at ordinary temperatures without any apparent combination, but on heating gently the reaction becomes so violent, because of its exothermic nature, that it can scarcely be controlled. On feeding the ground ore into heated acid, moreover, the product solidifies before complete decomposition is accomplished; if a large excess of acid is used to overcome this difficulty, the process becomes uneconomical. To overcome these difficulties, a mixture of comminuted ilmenite and strong sulfuric acid was fed continuously into a primary zone where the reaction was initiated by adding a small amount of water, steam, or dilute acid, or by heat. Once started, the reaction proceeded indefinitely as fresh charges were added, particularly if the acid component consisted of oleum and dilute acid liquor. This partially reacted mass, in the form of a semifluid paste, was moved continuously into a second zone held at an elevated temperature where combination proceeded to completion and solidification was effected. The product was subjected to attrition as it was moved forward, and it was discharged as a granular solid.

In a typical operation, oleum was mixed with 55° Bé sulfuric acid in such proportions that a 91 per cent acid at 70° C. resulted. One and one-half parts of this product were mixed with one part finely ground ilmenite (54 per cent titanium dioxide) and run into the first chamber, where the reaction was initiated by heat. It then overflowed into a second zone where the temperature was 180° C. In another example the ore (61 per cent titanium dioxide) and 93 per cent sulfuric acid were added continuously to the initial zone and moved forward as before. The operation could be carried out in a rotary kiln, a conveyor arrangement, or a series of pans. According to a similar process, applicable both to ilmenite and titanium-rich residues or muds obtained as by-products in vari-

ous steps of the commercial manufacture of pigments (from ilmenite), the attack was carried out in such a manner that the reaction mixture was always in the dry or lumpy state, thereby ensuring the elimination of all operating difficulties arising from a change in state during the operation.[106] Finely ground ilmenite or mud was mixed on a conveyor with solid iron and titanium sulfates from a previous operation, and enough sulfuric acid was added to complete the reaction. The proportions of ingredients of the mix were adjusted so as to obtain a solid granular product before the titaniferous material had combined with the acid, and this granular material was then fed continuously into a revolving, gas-fired kiln in which the reaction took place. Temperature of the reacting zone was held at 180° C. The reacted mass discharged from the kiln was crushed and ground, and a considerable proportion, around 20 per cent, was returned to the conveyor to be mixed with more ilmenite or mud and acid. An advantage of the process is that dilute acid can be used to effect the decomposition. If a comparatively weak sulfuric acid is used, however, it is necessary to lower the rate of solid feed to the kiln and to increase the amount of decomposed product recirculated in order to have sufficient acid for complete reaction after the water has been driven off in the feed end of the kiln. In such cases temperatures above 180° C. may be employed to effect faster evaporation.

In an example, the material used was a mixture of 114 parts of wet cake from filtering ilmenite solution, which contained 49.5 per cent solids and 23.1 per cent titanium dioxide on a wet basis, and of a dry material containing 44.2 per cent insoluble titanium dioxide and 23.8 per cent iron as oxides. This was slurried with 135.4 parts of sulfuric acid as fresh acid and the suspension was divided into three equal batches. The first portion was heated at 180° C. and then crushed and added to the second. This mixture was baked, after which a portion was again baked with the third batch of the original slurry. The final product was a dry mass which gave an over-all recovery of soluble titanium dioxide of 56.6 per cent.

An improved process consisted of acting on ilmenite with sulfuric acid in a continuous manner under such conditions that the ore-acid mixture was broken up into films which were later subjected to attrition.[107] In this manner any solid reaction product which englobed the particles of untreated ore were broken away so that fresh surfaces were exposed continuously to the action of the acid, and the inert bodies (balls) upon whose surfaces the films were deposited acted as heat stabilizing agents in that they disseminated

the heat of reaction and prevented local overheating. On the other hand, their residual heat initiated the reaction of the incoming mix.

The most convenient apparatus for carrying out the attack was found to be a tubular ball mill which could be operated continuously. Ilmenite and sulfuric acid in reactive proportions were fed in at one end and the rotation of the mill was so regulated that the reaction product emerged at the discharge end as a solid, disintegrated mixture of soluble sulfates of the base constituents of the original ore.

In a typical operation, ilmenite containing 53 per cent titanium dioxide and 33.3 per cent iron in the form of both ferrous and ferric oxides was employed. The oleum was 104 per cent sulfuric acid, and the amount used in the feed was 1.33 times the weight of titanium dioxide in the ore. This mixture was fed continuously from the agitated tank to the ball mill at a rate of one-half pound a minute, and at the same time steam was admitted to initiate the reaction. Decomposition started almost immediately and the steam was shut off. The reaction was kept going by the addition of dilute acid liquor recovered from the hydrolysis of a titanium sulfate solution which contained 23 to 25 per cent sulfuric acid and 8 g. per liter titanium expressed as the dioxide. The rate of addition of the liquor was held constant at 6.4 pounds per hour, and with this dilution the average concentration of the acid available for reaction was 82.4 per cent. A composite sample of the solid ball mill discharge gave, as soluble constituents, 18.9 per cent titanium dioxide, 11.0 per cent iron, and 15.3 per cent sulfuric acid in excess of that required to form soluble titanic and ferric salts. Recovery of titanium was 88.5 per cent.

Employing a pugmill attack, pulverized ilmenite and oleum in predetermined proportions were continuously added to an agitated tank and the mixture was allowed to flow into the feed end of a rotary screw conveyer.[108] Simultaneously with the acid-ore mixture, water or dilute waste acid was fed into the conveyer. At once heat was developed, and the exothermic reaction between the acid and ore was initiated. The mass gradually thickened as the reaction proceeded, and it was moved forward by adjacent and cooperatively acting helicoidal parallel screws rotated at different speeds and adapted to prevent accumulation of reacted material. The temperature was easily controlled by varying the speed of rotation of the paddle shafts and by varying the amount of diluent. Best results were obtained by operating under such conditions that the mass became dry in the first half of the conveyer length. Instead of using oleum and an aqueous diluent, 90 per cent sulfuric acid could also

be added at the start, but in this case the reaction had to be initiated by maintaining the feed end of the apparatus at an elevated temperature.

To illustrate, 3340 pounds of finely ground ilmenite containing 53 per cent titanium dioxide and 5000 pounds of oleum (104.5 per cent sulfuric acid) were fed per hour into a mixing tank. This overflowed into the conveyer, where the reaction was started by adding water, and a switch was then made to dilute waste acid (24 per cent sulfuric acid) which was then admitted at the rate of 1800 pounds per hour. The mass was continuously moved forward by the conveyer and discharged at the opposite end as a solid reacted mass.

Similarly, on treating finely ground ilmenite with 80 per cent sulfuric acid at 65° C. in a rotary kneading machine heated by an oil jacket, a vigorous reaction took place with the formation of soluble sulfates of the base components of the ore.[109] As soon as the reaction had subsided, the temperature was raised gradually to 250° C., and kneading was continued until the initial pasty product solidified to a dry crumbly mass consisting primarily of titanium and iron sulfates. Ninety per cent sulfation was readily effected by this process. The sulfates formed were dissolved by leaching the cake with water or dilute sulfuric acid.

In carrying out the continuous reaction of ilmenite with sulfuric acid on an endless conveyer, Moran and Nelson[110] found that a layer of a mixture of paper pulp and asbestos protected the steel belt employed and prevented the digestion reaction product from adhering, so that it could be discharged continuously from the surface of the protective layer.

Dissolution of the Digestion Product

Regardless of the method employed, the reaction product obtained by digesting finely divided ilmenite with strong sulfuric acid is leached with water or dilute sulfuric acid to obtain a solution consisting primarily of titanic, ferrous, and ferric sulfates, with minor proportions of sulfates of vanadium, chromium, manganese, and other metals, and of phosphates, depending upon the original composition of the ore. If the digestion is carried out so as to produce a porous cake, dissolution may be effected directly in the cylindrical, conical-bottom reaction tank without breaking up the mass by mechanical means. In such cases the leaching liquor is introduced at the bottom of the porous mass. Obviously the tem-

perature should be held relatively low (well below the boiling point) to avoid hydrolysis, but at the same time it should be maintained as high as practical to speed the rate of solution. To avoid possible loss of titanium, resulting from hydrolysis while dissolving the soluble sulfates from the reaction mass, Farup [111] employed dilute solutions of sulfuric acid as the solvent instead of water. This method was also followed by Washburn [112] and others. In general, it has been found desirable to employ dilute sulfuric acid for the initial leaching, followed by water in the later stages. Dangers of hydrolysis may be minimized by adding the solvent liquor in relatively small portions so as not to cause excessive dilution of the dissolved titanium sulfate, particularly in the initial stages.

Dissolution of the sulfate cake may be accelerated by maintaining a low concentration of trivalent titanium [113] during the operation, and this practice is usually followed. Agitation of the solution is necessary, since it contains suspended particles of the reaction product as well as some unreacted ilmenite which would tend to settle out in the tank and resist the solvent.

For reasons of economy the concentration of the final solution should be as high as is consistent with efficient operation, although the upper limit for practical handling is determined by the viscosity and the tendency toward crystallization. This value in general is around 8 to 10 per cent titanium dioxide. Such liquors always carry a small proportion of unreacted ore, siliceous residue, and gangue material in suspension, in more or less colloidal condition.

Reduction of the Solution

All the ferric component of the final ilmenite solution is reduced to the ferrous state, and to prevent later reoxidation during processing the treatment is continued until a small proportion of the titanium has been converted to the trivalent condition. Ferrous sulfate is more stable in solution than is the ferric salt, and it thus minimizes the precipitation of iron compounds along with the titanium oxide during the hydrolysis and washing steps. Furthermore the intrained ferrous salts are more easily removed from the hydrous titanic oxide pulp by washing than are ferric salts, since the latter have a strong tendency to change over to insoluble basic compounds or oxides as the acid concentration of the liquor is reduced.

In the earlier days of the industry, reduction was effected in the cathode compartment of an electrolytic cell, the anode compartment of which contained dilute sulfuric acid. Electrolysis was continued

until all the ferric ions and a small part of the titanic ions were reduced to the divalent and trivalent states, respectively.[114] Such solutions were also treated in a cell containing an unglazed porcelain compartment filled with 30 per cent sulfuric acid in which the lead anode was mounted. The ilmenite liquor was circulated through the cathode compartment until all iron compounds were reduced to the ferrous condition and enough titanous salts were produced to prevent reoxidation of the iron salts during subsequent treatment.[115] Later work showed that good yields of titanous ions could be obtained without the use of a diaphragm in the electrolytic reduction of such a solution.[116]

Weintraub [117] reduced the iron component of ilmenite liquors to the ferrous condition by introducing metallic zinc, sulfurous acid, or sodium thiosulfate, although metallic iron has been reported to give best results.[118] Employing metallic iron or its alloys [119] as reducing agents, greater efficiency was obtained at concentrations of 93 g. to 130 g. per liter titanium dioxide and at temperatures around 60° C. Krchma [120] reduced such solutions by introducing two metals in discrete form, such as tinned iron, which are between hydrogen and calcium in the electromotive series. For reasons of economy, iron is usually employed in large-scale operations. Supported in lead baskets, it may be introduced into the hot solution to effect reduction.

Rau and Swartz [121] employed sponge iron, produced by the reduction of ilmenite or titaniferous magnetite, to reduce the sulfate solutions for hydrolysis. The agent was added in small increments with agitation, and the temperature of the solution was held just below 60° C. Use of the titanium-bearing sponge instead of scrap iron resulted in an increase in the titanium to iron ratio in the solution and conserved sulfuric acid.

Ryan and Cauwenberg [122] circulated the ilmenite solution through or over the reducing agent at such a rate as to avoid overheating or local change in acidity factor. More stable solutions were obtained by this method.

Instead of treating the entire body of ilmenite solution with metallic iron until a small amount of trivalent titanium was formed, a small proportion was removed and its constituents were reduced as far as practicable. This solution, rich in titanous salts, was added back to the main batch of liquor, in slight excess of that required to convert all ferric iron to the ferrous state, so as to furnish a low concentration of titanous ions to the final mixture.[123] This operation may be carried out in a cyclic process. The required amount of

water and trivalent titanium solution were added to the reaction product of ilmenite, with sulfuric acid to dissolve the mass and reduce the ferric iron to the ferrous state. The reduced solution was then run into a settling tank where it was separated from insoluble matter by decantation, and the clear overflow was led to storage tanks for future use. The residue was withdrawn from the bottom of the tank and reslurried in another tank with dilute titanium sulfate solution. Muds from this tank, which contained much less titanium than those from the first settling operation, were discharged to waste. If economic considerations warrant, however, more titanium can be recovered by employing a third settling stage. Wash liquor obtained as a clear overflow from the second tank contained 70 g. titanium dioxide, 50 g. ferrous iron, and 250 g. total sulfuric acid per liter. This solution was treated with tin scrap at 30° to 50° C. to reduce the titanium to the trivalent state. An efficiency of 90 to 95 per cent was obtained, and 0.38 pound of tin scrap was used for each pound equivalent of titanium dioxide reduced. After reduction the titanous solution was added to the reaction vessel to reduce the ferric iron and act as a solvent for fresh digestion cake. The proportion used was such that the final solution contained a slight excess of the trivalent titanium to accelerate dissolution and to compensate for air oxidation in subsequent operations. The method was also applicable to scrap iron as the reducing agent, but wash liquors of higher concentration (75 to 80 per cent) were required to obtain satisfactory efficiency. Mechanism of the reduction may be expressed by the following equations:

$$Fe + 2Ti(SO_4)_2 \rightarrow FeSO_4 + Ti_2(SO_4)_3$$
$$Fe_2(SO_4)_3 + Ti_2(SO_4)_3 \rightarrow 2Ti(SO_4)_2 + 2FeSO_4$$
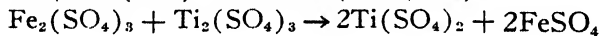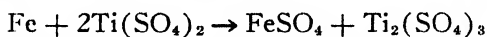
Reduction may also be effected by adding titanous sulfate in crystalline form.[124] This method has the advantage in that it is practically instantaneous and does not introduce foreign materials into the solution. Any other soluble titanous compound whose acid radical does not interfere with subsequent treatment may be employed.

Brooks [125] treated ilmenite solutions with sulfur dioxide in the presence of activated carbon to effect reduction of the ferric component to the ferrous condition. In a specific application, to 100 parts by weight of a sulfate solution of ilmenite was added 0.18 part activated carbon made from wood or vegetable products, and 100 parts sulfur dioxide gas was then passed through at a temperature of 30° C. for 2 hours. Ninety per cent of the ferric sulfate was reduced to the ferrous condition. Employing the same condi-

tions without the carbon (gas was passed through at the same temperature for the same time) only 3.1 per cent of the total ferric iron was reduced. Scrubbing towers may be used to advantage.

The proportion of the titanium component that should be converted to the trivalent state has been reported as high as 5 per cent,[126] although much lower values, 1 or 2 per cent, have given satisfactory results. Obviously it is only necessary to have a high enough proportion of this agent to maintain reducing conditions throughout the processing operation. Large excess should be avoided since it is not precipitated in the hydrolysis step, and, furthermore, reoxidized titanous sulfate tends to yield discolored oxide.

Clarification of the Solution

At this stage filtration by conventional methods would be unsatisfactory, for the solution is strongly acid and contains finely divided suspended materials that are at least in part in the colloidal condition. Since ordinary filter materials are either attacked by strong acid or clogged by the mud, the liquor is generally subjected to a primary clarification process. The colloidal material is first coagulated by the conventional method of introducing a second colloid of opposite electrical charge, such as glue or a metallic sulfide, after which the liquor is passed through a series of settling tanks and finally passed over a specially designed plate or rotary filter coated with an acid-resisting material such as diatomaceous earth (precoat), nitrated cloth, glass cloth, vinyl-resin cloth, or perforated rubber sheets. Instead of relying on the force of gravity, centrifuging or reduced pressure may be employed to speed up the operation.

According to Goldschmidt,[127] the suspended solids in sulfate solutions of ilmenite are electropositive colloids that settle rapidly on neutralization of this charge by precipitated sulfur, which is electronegative. The colloidal sulfur may be precipitated in the solution by the oxidation of hydrogen sulfide by a ferric salt or by sulfur dioxide. Rapid settling of the suspended material may also be effected by the addition of organic colloids having an electrical charge of opposite sign. Glue, albumen, and casein have been found to be particularly effective. On mixing a small proportion of the agent into the suspension, the solids are rapidly coagulated and settled, leaving a clear supernatant liquor which is decanted or filtered or both. In an example, 2 or 3 decigrams of noncoagulated albumen were added per liter of sulfate solution having a specific gravity of 56° Bé, with

thorough mixing. After standing for 24 hours, the clear supernatant liquor was decanted and the muddy residue was filtered.[128] Rapid settlement was also effected after treating the slime products with gelatin [129] in a similar manner.

Frequently glue and similar organic colloids fail to remove the suspended materials as completely as desired, and at least part of the coagulating agent remains in the solution. Glue, for example, may cause frothing in a later step, and on standing it is also subject to decomposition or putrefaction. In an improved process, glue, gelatin, alginates, albuminoids, proteins, or dextrin were added to hasten the settling of the suspended solids as before, and the partially clarified solution was then treated with a mutually coagulating organic colloid, particularly tannins, which removed any added material as well as any original colloid remaining in suspension in the solution.[130]

As an example, a concentrated solution containing 1 kg. of glue was added to 1 cubic meter of liquor obtained by dissolving ilmenite in sulfuric acid. After primary settling, the solution which carried in suspension 0.04 per cent inorganic impurities and practically all the glue added was treated with 2.5 kg. of tannic acid as a concentrated aqueous solution. The tannic acid coagulated the glue to form flocs which settled rapidly and carried down with them the remaining suspended material. Such solutions have also been coagulated and clarified by adding gelatin or glue of animal origin, together with a light, solid material such as sawdust or asbestos,[131] or by treatment with an extract of flaxseed or its husks.[132]

Solutions of titanium which are difficult to filter may be clarified by mixing in colloidal metallic sulfides having an electric charge opposite in sign to that of the suspended matter to be removed. Heat may be applied to reduce the viscosity if necessary. After settling, the supernatant liquor is separated by decantation or filtration or both. In an example, a sulfate solution of ilmenite, of specific gravity 50° Bé and containing 200 g. per liter titanium dioxide, was brought to 50° C., and 0.5 g. arsenious oxide, as a soluble salt dissolved in water, was added per liter. Solid ferrous sulfide sufficient completely to precipitate the arsenic as sulfide was then introduced. Flocs immediately formed and the suspension could be filtered immediately, or, after standing, the supernatant liquor could be decanted from the residue. The proper amount of dissolved arsenic may be introduced into the solution by adding arsenious oxide to the ilmenite-sulfuric acid mixture before digestion.[133] To effect coagulation,

a sulfide was added to the solution to precipitate the arsenic as sulfide.[134] Zhukova[135] treated such solutions with copper sulfate and sodium sulfide to effect clarification. The copper sulfide formed, which was colloidal in nature, neutralized the charge on the suspended solids so that coagulation and settling were effected rapidly. In this process the composition of the solution was important, since titanous ions reduce copper sulfate to metallic copper. Concentrated solutions may be clarified by a two-stage process consisting first of sedimentation, followed by centrifugal separation at 40° to 90° C.[136]

Filtration

Instead of employing the time-consuming clarification process for ilmenite liquors, Weise and Raspe[137] filtered such solutions directly through nitrated cellulose cloth. Trivalent titanium compounds should not be present, however, since they cause a slow denitration of the fabric, particularly at elevated temperatures. In the operation of the process, the sulfate solution was first reduced with scrap iron to a point just short of the formation of trivalent titanium and was then filtered through the nitrated fabric, after which the reduction was further carried to the desired stage by electrolysis or by adding titanous salts directly. For example, 100 kg. of ilmenite in a finely divided state was intimately mixed with 200 kg. of 80 per cent sulfuric acid and heated at 150° C. for 1 hour. Water was added to the reaction product in such proportions as to obtain a solution of 1.45 specific gravity. Metallic iron was then introduced, with stirring, at 70° C. until ferric ions just disappeared. At this point the reduction was interrupted, and after cooling to 40° C. the solution was passed through a filter press, the cloths of which consisted of nitrated cotton. Luttger[138] recommended Vinyon cloth as coating for continuous filters. Macerated paper pulp, deposited from a water suspension on perforated sheet lead, has been used successfully.[139] In a continuous process, a drum, coated with a porous filter media such as diatomaceous earth, was revolved at 700 r.p.m. in the solution to be filtered. At each revolution of the drum a cleaning element or blade removed the accumulated slimes, together with a thin layer of the filter material.[140]

Filtration of such solutions, whether first clarified or not, was facilitated by stirring diatomaceous earth or a similar filter aid into the hot acid-bearing liquor.[141] Lewis[142] found that the filtration rate was increased by adding 1 gallon of sulfonated oil to 10,000 to 20,000 gallons of the crude solution.

Purification of the Solution

By the generally employed method of manufacture, some ilmenite ores, for example those occurring in Virginia, tend to yield pigments sensitive to light and of unsatisfactory color. These undesirable properties are the result of impurities, such as chromium and manganese compounds, derived from the ore, and are either dissolved or colloidally dispersed in the sulfate solution so that they are precipitated along with the titanium dioxide in the hydrolysis step. Very small proportions of these impurities are sufficient to render the pigment photosensitive and off color. These injurious manganese and chromium compounds may be effectively removed from the solution by adsorption on gypsum or strontium sulfate, just after the crystallization step.[143] Hydrous titanium oxide precipitated after this treatment yielded a pigment of good color and high stability to light.

To illustrate, a regular sulfate solution of Virginia ilmenite, after the crystallization stage, was mixed with 9 per cent of its weight of ground gypsum and agitated for 12 hours at room temperature, after which it was filtered to remove the gypsum together with the adsorbed impurities. The filtrate having been processed in the usual manner, the finished pigment had excellent color and was not photosensitive. These undesirable impurities were also removed from solutions of this type by treatment with nonsiliceous adsorbents such as activated carbon and cotton fibers.[144] The impurities adsorbed on the added agents were removed by filtration.

Bachman[145] treated clarified solutions with potassium ferricyanide or potassium ferrocyanide to precipitate undesirable impurities, and then boiled the diluted filtrate to effect hydrolytic precipitation of the titanic oxide of improved purity.

Sulfate solutions stable to premature hydrolysis[146] may be produced from ores having a high iron to titanium dioxide ratio by adding dried precipitated titanic oxide before the sulfuric acid attack. In an example, the ratio was adjusted to 0.72. Such solutions, after removal of ferrous sulfate by crystallization, may be recycled to the dissolving step to increase the iron to titania ratio.[147]

The acidity of sulfate solutions of ilmenite may be reduced without disturbing their crystalloidal properties by adding ferrous carbonate[148] or metallic sodium or potassium[149] at a temperature not higher than 60° C. The same results were obtained by treating the solution with a neutral, soluble, organic extracting agent such as a ketone, alcohol, ester, or cyclohexanone.[150] The mixture was

agitated and allowed to settle, after which the upper layer, rich in acid, was drawn off for recovery of the organic agent by vacuum distillation. By another modification, hydrogen peroxide or barium peroxide was added to the solution to oxidize the ferrous iron to the ferric state and thereby tie up a larger quantity of sulfuric acid.[151]

Grachev[152] found it feasible to remove iron and aluminum from ilmenite solutions by electrolysis, employing a ceramic diaphragm and lead electrodes. Lead compounds were removed by adding barium or strontium hydroxide to the solution.[153] The precipitate of barium sulfate, which adsorbed the lead component, was removed from the solution by settling or filtration.

By gradually diluting impure titanium salt solutions with water, impurities such as vanadium, columbium, and tantalum were precipitated progressively.[154]

Removal of Ferrous Sulfate by Crystallization

Sulfate solutions of ilmenite contain practically all the iron of the original ore. After reducing this component to the ferrous state, the solutions, on cooling to room temperature, still carry an appreciable amount of iron, depending upon the initial concentration. This large proportion of ferrous salt may be a source of trouble in subsequent operations. Sulfuric acid, liberated on hydrolysis, reduces the solubility of the ferrous sulfate, and crystals may become mixed with the titanium dioxide. On the other hand, dilution for overcoming this factor would increase the cost of recovering the sulfuric acid. These disadvantages can be avoided if the iron content is first reduced by cooling the solution to subatmospheric temperatures, 5° to 15° C. This temperature may be attained conveniently by a process of forced evaporation. Heptahydrated ferrous sulfate crystallizes out without forming a double salt with the titanium, and the crystals may be separated by decantation, filtration, centrifuging, or a combination of these, with practically no loss of titanium salts. The mother liquor may then be concentrated to relatively high titanium content without excessive thickening, and the sulfuric acid liberated on hydrolysis may be recovered more economically.[155] Furthermore, in certain methods of hydrolysis, particularly that of Blumenfeld, the ratio of titanium to iron must be adjusted to within specific limits for best results. On the other hand, solutions from which too large a proportion of iron has been removed may give pigments of unsatisfactory properties. For this type of hydrolysis crystallization is generally carried to such a stage that the content of ferrous sulfate is approxi-

mately 0.9 that of the titanium dioxide.   By employing other methods of hydrolysis applicable to lower total concentration, however, it may not be necessary to remove any of the ferrous sulfate, as, for example, in the precipitation of composite pigments.

Concentration of the Solution

Concentration of the crystallized mother liquor is effected by evaporation under reduced pressure at a correspondingly low temperature to prevent premature hydrolysis at this stage.[156] However, solutions for the manufacture of the relatively pure titanium dioxide by certain methods, and of coalesced composite pigments in general, are normally not crystallized or concentrated.

Chapter 11

HYDROLYSIS OF TITANIUM SULFATE SOLUTION

The exact mechanism for the thermal hydrolysis of titanium salt solutions has not been definitely established, although the simplified form of a proposed scheme is presented here as an indication of the process.[1] A titanic ion in solution, having a coordination number of 6 in accordance with Werner's theory of complexes, may be regarded as attached to 6 water molecules by these secondary valence bonds. The first stage of hydrolysis would then be the splitting off of a hydrogen ion from one of the water molecules, leaving a titanium complex with 5 aquo groups and one hydroxo group, thus lowering the charge by 1 unit.

$$\begin{bmatrix} H_2O & & H_2O \\ & \diagdown \diagup & \\ H_2O - & Ti & - H_2O \\ & \diagup \diagdown & \\ H_2O & & H_2O \end{bmatrix}^{++++} \longrightarrow \begin{bmatrix} H_2O & & OH \\ & \diagdown \diagup & \\ H_2O - & Ti & - H_2O \\ & \diagup \diagdown & \\ H_2O & & H_2O \end{bmatrix}^{+++} + H^+$$
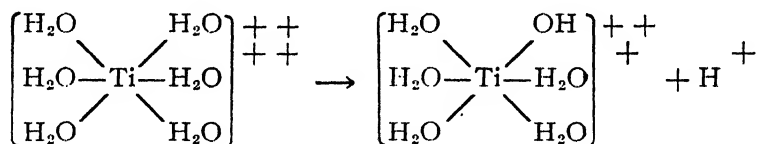
Further reaction would result in the combination of 2 such units through the hydroxo groups, with the splitting out of 2 molecules of water to form a dinuclear titanium ol-complex. The ol group or bridge is a hydroxyl shared by 2 nuclear titanium atoms, and would be unsatisfied as shown in the following structural diagram:

$$\begin{bmatrix} & & H & & \\ & & O & & \\ & & \diagup \diagdown & & \\ (H_2O)_4 - Ti & & & Ti - (H_2O)_4 \\ & & \diagdown \diagup & & \\ & & O & & \\ & & H & & \end{bmatrix}^{++++++}$$
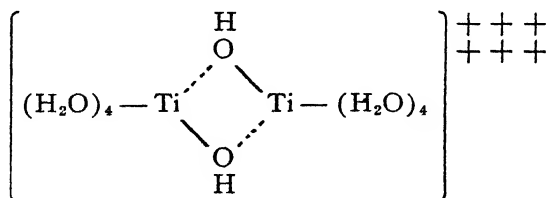
This ol complex would in turn lose 2 hydrogen ions from the hydroxo groups, thus producing a more stable oxo linkage, and the resulting oxo complex would have 2 fewer positive charges.

$$\left[(H_2O)_4 - Ti \begin{array}{c} O \\ \diagup \diagdown \\ \diagdown \diagup \\ O \end{array} Ti - (H_2O)_4 \right]^{++}_{++} + 2H^+$$
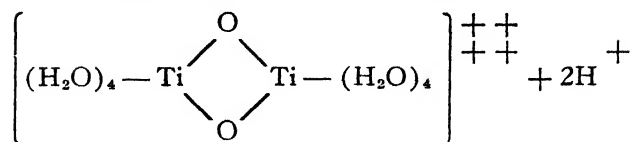
Such a compound with 1 ol and 1 oxo bridge would appear possible. Dissociation of additional water molecules to hydroxo groups in the dioxo compound or complex would render possible further combination to form tetraoxo compounds:

$$(H_2O)_4 - Ti \begin{array}{ccc} O & O & O \\ \diagup \diagdown & \diagup \diagdown & \diagup \diagdown \\ & Ti & Ti \\ \diagdown \diagup | \diagdown \diagup | \diagdown \diagup \\ O & O & O \end{array} Ti - (H_2O)_4$$
$$(H_2O)_2 \quad (H_2O)_2$$
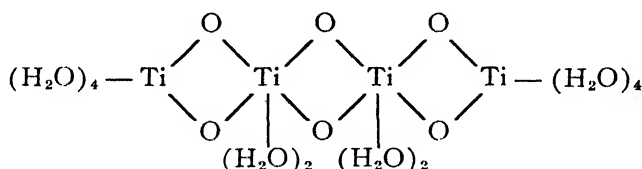
By progressive olation and oxolation, the building up of polynuclear complexes of titanium would result and these might be expected to join up to form chain- and cross-linked complexes of the type shown below:

$$(H_2O)_3 - Ti \cdots Ti - (OH_2)_4$$
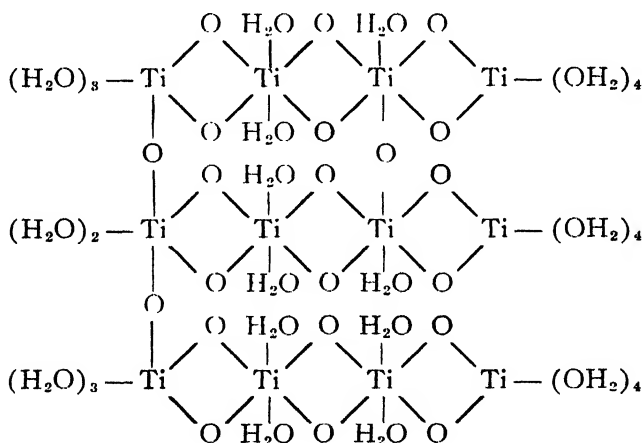
In any case, these grow in size until the colloidal state is reached, and finally precipitation begins. As a result the hydrolytic equilibrium is disturbed, a new quantity of colloidal titanium oxide is formed by decomposition of more of the crystalloid salt in solution, and this, in turn, is coagulated. The process continues until the greater part of the titanium is precipitated in the form of a relatively insoluble hydrous oxide.

Rigid control of the formation of colloidal hydrous titanic oxide and of the conditions during its subsequent coagulation is of primary importance in the manufacture of titanium dioxide of highest pigmentary properties. This has been mastered, at least in part, by extensive research.

The hydrous oxide precipitate obtained commercially by thermal hydrolysis of sulfuric acid solutions of titanium is probably made up of complexes of the type given before, but it also contains sulfuric acid within the nucleus. Experimental evidence indicates that this residual acid is not chemically combined but adsorbed on the hydrous oxides. At any rate it is closely held but can be driven off at temperatures in the neighborhood of 700° C.

Anatase and Rutile Modification of Titanium Dioxide

Normally, sulfate solutions on hydrolysis yield directly titanic oxide of the anatase crystal form, while halides and nitrates give rutile. Under special conditions, however, the results may be reversed. For example, by seeding sulfate solutions with rutile nuclei all the titanium content may be precipitated in this form. Furthermore, solutions prepared by dissolving in sulfuric acid the hydrous oxide originally precipitated from aqueous titanium tetrachloride have been reported to yield directly an oxide having the rutile structure.

On the other hand, titanium tetrachloride and other solutions which normally yield oxides of the rutile crystal modification may be hydrolyzed in the presence of phosphoric and sulfuric acids to give anatase.[2] For example, on hydrolysis of a 20 per cent solution of titanium tetrachloride, after addition of 5 per cent or more sulfuric acid based on the titanium dioxide, anatase rather than rutile was obtained. On the other hand, the hydrolysis product of sulfate solutions to which sodium chloride had been added was anatase rather than rutile. These results were confirmed by Parravano and Caglioti,[3] who found that hydrochloric acid solutions on hydrolysis yielded titanium dioxide which showed the rutile structure initially, but, if phosphate or sulfate radicals were present, anatase was formed first but converted to rutile on further heating.

According to Weiser and Milligan,[4] hydrous titanium dioxide freshly precipitated from sulfate solutions at room temperature gave no X-ray diffraction lines or bands, although the anatase structure was developed after aging under water for several months at room temperature or on heating to 184° C. The product precipitated at

100° C. gave X-radiograms of anatase directly. Hydrous oxide formed by the hydrolysis of boiling solutions of titanium tetrachloride or tetranitrate had the structure of rutile, while that precipitated from sulfate solutions under the same conditions gave the X-radiograms of anatase. Thermal dehydration isobars and X-ray analysis of the different products indicated that the water was given off continuously and that no definite hydrate of titanium dioxide has been prepared. Products obtained by igniting at 1000° C. the hydrous oxide precipitated in the cold from sulfate solutions showed the rutile structure.

The transition from anatase to rutile structure [5] has been reported to take place at 800° to 1000° C., depending on the conditions of precipitation from titanium sulfate solutions and upon the nature of the impurities. According to the same workers,[6] the appearance of a yellow color on calcination is due to the presence of impurities and has no connection with the transformation from anatase to rutile structure. Sufficiently pure samples remained white or became slightly grayish. According to Parravano and Caglioti,[7] stable anatase was precipitated from sulfate solutions with high acidity and high titanium dioxide content, while at low titanium dioxide concentration and relatively low acid ratio the product obtained was a mixture of anatase and rutile at temperatures up to 830° C., but it was converted completely to rutile after 1 hour at 850° C. Hydrolysis under ordinary conditions of a sulfate solution containing 8.1 per cent titanium dioxide and having an acidity factor of 1.28 yielded a precipitate which retained the anatase structure at 900° C., but if a wet hydrolysis product which would itself form rutile on ignition was added as a seeding agent, the titanium dioxide precipitated showed the rutile structure after calcination at 900° C. for 1 hour.

Thus the nature of the calcined material was strongly influenced, not only by the initial concentration of the solution, but also by the temperature, and, finally, by the rate of hydrolysis. For example, a solution containing 5.12 per cent titanium dioxide at acidity factor 1.07 hydrolyzed on long standing to give a product that was anatase after calcination at 950° C., but higher temperature hydrolysis gave a precipitate which converted to rutile by the time it reached 950° C.

Oxides and hydroxides of titanium may be transformed readily to the rutile modification by heating in the presence of small proportions of a number of agents such as zinc oxide, lithium chloride, aluminum sulfate, magnesium sulfate, barium sulfate,[8] antimony oxide,[9] or mixtures of these. Zinc oxide, which is representative of the group, forms solid solution with the titanium dioxide and dissociates at higher temperatures. At the temperature of dissociation,

rutile is separated and the zinc oxide reacts with more anatase so that the process is continuous and large amounts of rutile may be converted by small amounts of the agent. Good results may be obtained with as low as 0.5 per cent zinc oxide based on total solids, and 2.0 per cent was very effective. Conversion was inhibited by the presence of phosphates and compounds of the alkali metals.

Titanium oxide of the anatase structure may be redissolved either directly or indirectly to form halide, nitrate, or chloroacetate solutions, and then reprecipitated from such solutions in the rutile form. Though these methods are indirect, they may be carried out in a cyclic process so that the reagents are recovered and used over and over again. For instance, hydrous anatase pulp may be heated with aqueous barium hydroxide to form the titanate, which is readily soluble in nitric or hydrochloric acid.

Sulfate solutions may be converted to chloride solutions, which yield titanium dioxide of the rutile crystal form directly by adding barium chloride or other compounds which yield insoluble sulfates.

Precipitation with Alkaline Agents

In the very early stages of the industry, the titanium component was selectively precipitated from solution as hydroxide or hydrous oxide by adding controlled amounts of alkaline reagents, but this gave products which were of poor color and undesirable in other respects. Thermal hydrolysis of dilute sulfuric acid solutions containing 3 to 5 per cent titanium dioxide gave pigments of better quality, but the method was slow and uneconomical. Practically pure titanium dioxide was obtained by a process based on the method of producing coalesced composite pigments. A small proportion of anhydrite was suspended in the original solution, and after hydrolysis the calcium sulfate was removed from the precipitate by washing. This was effective because of the much greater solubility of calcium sulfate than of the titanic oxide in water. Although pigments of good quality were obtained, the process was slow and costly.

The next real advancement was the development of a process by which titanium oxide was precipitated by heating more concentrated solutions (80 g. to 350 g. per liter titanium dioxide), in which the content of sulfuric acid was so regulated that the titanium was present not as a normal salt, but rather as one having a sulfate content between that corresponding to the titanyl and normal salts. Such concentrated acid-poor solutions yielded pigments of good quality, but complete hydrolysis required prolonged boiling under normal

conditions or heating for much shorter periods in an autoclave at higher temperatures corresponding to superatmospheric pressure. The high concentrations had the additional advantage of permitting economical recovery of the sulfuric acid from the hydrolysis liquor.

To hasten precipitation under atmospheric conditions, various nucleating agents or seed were added to the hydrolysis solution, and in most cases these consisted essentially of a suspension of colloidal titanium oxide. Further developments involved a slow admixture of concentrated, acid-poor ilmenite solution with hot water in such a manner that seeding agents were formed directly within the main body of the hydrolysis mixture.

Other specialized processes have been reported, and among the more important of these are methods of producing rutile directly from sulfate solutions.

Dilute Solutions

One of the earliest commercial methods for the hydrolytic precipitation of titanium oxide of high purity was developed by Weintraub.[10] Finely ground ilmenite was decomposed quantitatively with concentrated (93 per cent) sulfuric acid, employing no excess over the theoretical amount required to form normal salts with the base constituents. Heat to initiate the reaction was supplied by live steam. The reaction product was dissolved in water. All the iron component was reduced to the ferrous condition by introducing metallic zinc, sulfurous acid, or sodium thiosulfate. And the solution was clarified, diluted, and boiled to effect hydrolytic decomposition. The precipitate was filtered, washed, and calcined to obtain titanium dioxide of high purity. Alternatively, a product of somewhat less purity was obtained by throwing the solution into a large quantity of boiling water. Weintraub was primarily concerned with preparing pure titanic oxide for arc lights and other electrical uses, and was not interested in or failed to recognize the possibility of this compound as a white pigment.

Rossi and Barton [11] developed one of the earliest methods of producing relatively pure titanium oxide of pigment grade which involved the hydrolytic decomposition of very dilute sulfate solutions containing iron and other impurities. The reaction product of ilmenite with 95 per cent sulfuric acid in a proportion 2.5 times the titanic oxide content was dissolved in three times its volume of water, and all iron was reduced to the ferrous state by electrolytic means. This solution was clarified, diluted to 0.5 to 3 per cent titanium

dioxide, and boiled for 15 to 30 minutes to effect hydrolysis. The precipitate was washed and dried at 100° C. to obtain a product containing 70 to 90 per cent titanium dioxide, 5 to 10 per cent sulfur trioxide, and 5 to 20 per cent closely held water. It was then calcined to drive off the remaining water and acid and effect crystallization.

Basic Solutions

To facilitate hydrolysis, Barton [12] treated solutions of this type with calcium or barium hydroxide to reduce the sulfuric acid-titanium dioxide ration to a value less than that corresponding to the normal sulfate, but short of that required to yield a precipitate of titanium. Such solutions were referred to as "basic." The insoluble residue was separated; the liquor was diluted to 3 per cent titanium dioxide equivalent, and electrolyzed without a diaphragm to reduce and maintain all the iron in the ferrous state. The solution was heated at 90° to 100° C. by live steam or by external sources to effect hydrolytic precipitation of the titanium, and recoveries of 85 to 90 per cent were obtained after heating for 2.5 to 5 hours. Under these conditions ferrous iron remained in solution. The precipitate was washed and calcined at 750° C. to give a practically pure titanium dioxide pigment. In addition to the above-named agents, part of the excess sulfuric acid was neutralized with calcium, barium, strontium, or lead carbonates, sodium hydroxide or carbonate, or benzidine in preparing solutions of this type. [13] Resulting precipitates of insoluble sulfates were filtered off, and the solution was subjected to thermal hydrolysis as before.

Hydrous oxide may also be precipitated by heating more concentrated solutions containing less than 2 moles of free and combined sulfuric acid per mole of titanium dioxide, and less than 55 per cent water by weight. [14] More dilute solutions may be concentrated by evaporation, or a liquid that does not enter into reaction with the constituents, such as glycerol, ethylene glycol, or aliphatic alcohols, may be added to take up the excess water. The process is also applicable to composite pigments. Weizmann and Blumenfeld [15] precipitated hydrous titanium oxide by heating sulfuric acid solutions of ilmenite to near the boiling point. The surface of the liquor was covered with a layer of oil or paraffin during the hydrolysis step to prevent evaporation. After separation of the precipitated titanium oxide, the filtrate was cooled to crystallize out ferrous sulfate, and the liquor containing sulfuric acid and some titanium sulfate was used in preparing a new batch of ilmenite solution.

Pressure Hydrolysis

The next step forward was a method developed by Fladmark,[16] according to which hydrolysis was effected by boiling at atmospheric pressure, or by heating at higher temperatures in an autoclave, more concentrated ilmenite solutions having a content of sulfuric acid between that corresponding to the titanyl and normal salts. These contained from 80 g. to 250 g. per liter titanium dioxide, and from 80 g. to 400 g. per liter sulfur trioxide, free and combined with titanium. Typical concentrations in grams per liter of constituents are given in Table 2.

TABLE 2

ANALYSES OF SOLUTIONS, GRAMS PER LITER

TiO_2	Fe^{++}	Fe^{+++}	SO_3	SO_3 Calculated as Equivalent	Shortage of SO_3
163.5	101.0	3.3	363	478.8	116.8
210.0	49.3	0.0	311	490.7	143.9
99.0	53.7	29.3	297	337.8	40.8
169.2	84.6	40.8	488	547.4	59.4

Ilmenite was decomposed with sulfuric acid in such proportions that the solution obtained by lixiviating the reaction product contained less acid than would be required by the titanium, iron, and other bases to form normal salts. All iron was converted to the ferrous state, and the clear, concentrated solution was hydrolyzed in a lead-lined vessel equipped with coils of lead pipe through which steam was passed for heating. This required boiling at atmospheric pressure for long periods of time, but the process was hastened by employing higher temperatures corresponding to autoclave pressures. The precipitate of hydrous oxide was washed and calcined to produce titanium dioxide of pigment grade. Sulfuric acid was recovered economically from the relatively concentrated hydrolysis liquor.

According to Specht,[17] the rate of hydrolytic decomposition of titanium sulfate and the properties of the products obtained are determined primarily by the absolute concentration of the solution, the free acid content, and the temperature employed. Best results were obtained by effecting hydrolysis under pressure of a solution of specific gravity 1.50 containing 35 per cent potential sulfuric acid (free and combined with titanium) at a temperature of 170° to 180° C. For this range of temperature the specific gravity could fluctuate between 1.55 and 1.35, and the potential or active acid

between 25 and 40 per cent. However, the specific gravity of solutions poor in titanium could be brought effectively within the specified range by adding neutral salts such as alkali metal sulfates. In a similar process, solutions of titanic sulfate containing free acid were hydrolyzed by heating to a raised temperature under pressure after treatment with 10 per cent crude precipitated titanic acid.[18]   .

Buckman[19] also observed that the speed of thermal hydrolysis of acid-poor ilmenite solutions increased with temperature. Higher working temperatures were obtained either by employing solutions of higher concentrations or by increasing the pressure above atmospheric. Although the first alternative was of limited application, because of the stability of such solutions, the second was accomplished by heating in an autoclave and temperatures far above the normal boiling point were reached. At around 100° C. the precipitates were usually slimy and dried to hornlike masses of low tinting strength, but at temperatures of 170° to 185° C. solutions of the same chemical composition gave precipitates of dense titanic oxide which dried to soft powders having very good covering power. Furthermore, the yields were much greater than those obtained by boiling in vessels open to the atmosphere. In an example, a concentrated solution of titanic sulfate containing a small proportion of free acid was heated to 180° C. in a gas-tight, glass-lined steel cylinder at the corresponding pressure for 20 minutes. The washed and calcined product gave a fine white powder of very high covering power. This method had the advantage that solutions of much higher concentrations could be hydrolyzed without precipitation of iron, and the time required was only one fifth to one tenth that required at atmospheric pressure. The method was also applicable to the production of composite pigments and to the hydrolysis of chloride solutions.

According to a related process, solutions in which the titanium was present as normal sulfate were heated under pressure to temperatures above the normal boiling point to effect hydrolytic precipitation.[20] The temperature required for decomposition depended upon the concentration of both free acid and titanic sulfate. A solution of specific gravity 1.30, containing 0.792 g. titanium dioxide and 0.0149 g. ferrous iron per cubic centimeter, was not completely decomposed on heating for 2 hours at 147° C., but complete precipitation was effected at 160° C. in 30 minutes. A solution of the same composition, diluted with water to a specific gravity of 1.10, threw down its entire titanium content after 30 minutes at 135° C. The

washed precipitate, dried at 110° C., contained 84 to 94 per cent titanium dioxide, 1 to 5 per cent sulfur trioxide, trace to 2 per cent ferric oxide, and 4 to 10 per cent water. Calcination at 550° to 600° C. was sufficient to effect removal of water and acid and develop pigment properties.

So-called "acid" solutions of titanic sulfate, that is solutions containing acid in excess of the amount required to form normal salts with the base constituents, were hydrolytically decomposed at lower temperature and pressure by adding small proportions of a solution of a basic salt having a mole ratio of sulfuric acid to titanium dioxide between 1.8 and 1.5.[21] The solution obtained by leaching the reaction product of ilmenite with 2 parts of concentrated sulfuric acid was treated with scrap iron or electrolyzed to reduce all ferric component to the ferrous state and then clarified. A large part of the ferrous sulfate was crystallized by cooling, and titanium was precipitated hydrolytically from the mother liquor by heating in an autoclave under a pressure corresponding to a temperature of 150° C. This hydrous titanium oxide was filtered, washed, and calcined to develop pigmentary properties. The ferrous sulfate was heated to produce sulfur trioxide which was led into the residual liquor to yield strong sulfuric acid for reaction with more ore.[22]

According to a method used by Oppegaard and Stopford,[23] 1000 g. ilmenite ore was mixed with 510 ml. of 93 per cent sulfuric acid and added to 370 ml. more of the 93 per cent acid at 130° C. in a cast-iron pot. The charge was heated with stirring to fumes of sulfur trioxide, and 40 ml. of water was added to initiate the reaction. After the reaction had gone to completion, the solid mass was baked for 30 minutes at 200° C., cooled, and dissolved in water at 60° C. The solution was adjusted to a specific gravity of 1.50, reduced with scrap iron to a titanous oxide content of 3 g. per liter, and clarified. It was then cooled to 27° C. to remove part of the ferrous sulfate by crystallization, and the mother liquor was concentrated by vacuum evaporation to a specific gravity of 1.60 and hydrolyzed in an autoclave by heating at a temperature corresponding to a superpressure of 20 pounds for 80 minutes. After thorough washing the pulp was treated with 0.60 per cent potassium carbonate, then calcined and finished in the usual manner.

Titanic acid unaffected by light was produced by hydrolysis, under pressure, of ilmenite solutions having all the iron component in the divalent state and a small proportion of the titanium in the trivalent condition. In an example, the presence of 0.02 to 0.04 per cent titanous ion was sufficient.[24]

Ilmenite solutions containing 2.6 to 6.0 moles of sulfuric acid per liter were hydrolyzed by heating in a closed container at 350° to 450° C., under pressures corresponding to this temperature.[25] The product was anhydrous crystalline titanium dioxide with well-developed pigment properties. Such solutions, to which sodium chloride had been added, were heated under pressure at 300° to 320° F. to obtain a hydrolysis product [26] which was filtered, washed, and calcined.

At any given temperature the rate of hydrolysis was found to increase with pressure.[27] For example, under a pressure of 3 to 11 atmospheres, reaction began at 80° C. and was complete at 100° C.

Added Nuclei

To hasten the rate of thermal hydrolysis of sulfate solutions at atmospheric pressure and at the same time obtain products of pigment grade, various nucleating or seeding agents have been added. Although many types have been proposed, these in general have been suspensions of colloidal titanium compounds, but have varied considerably in the method of preparation and in method of admixture with the solution to be hydrolyzed. Frequently very small proportions of such agents have proved effective, and rarely has more than 5 per cent been required to give optimum results.

According to Mecklenburg,[28] whenever titanic salt solutions are subjected to hydrolysis there is a certain induction period between the beginning of the operation and the first visible precipitation during which colloidal titanium oxide is formed. These particles serve as centers of accumulation as hydrolysis proceeds, and the result is the formation of agglomerates which produce a visible precipitate as coagulation continues. On heating such solutions near the boiling point, hydrolysis occurs with the formation of a precipitate of hydrous oxide and the liberation of an equivalent amount of acid. Dilute solutions are more easily hydrolyzed, but on the other hand the economic operation of the process requires the use of higher concentrations, since otherwise the free acid obtained as a by-product would be too dilute to permit its recovery at a profit. On addition of as little as 1 per cent nucleating suspension "seed," based on the titanium component, however, hydrolysis of strong solutions can be effected readily. At temperatures below 50° to 60° C. the mixture appears turbid, but above this range it passes through a clear stage; on further heating at 100° to 105° C. for 3 hours, more than 90 per cent of the titanium is precipitated. It appears probable that the

added titanium dioxide seed does not actually dissolve on heating, but is converted to a colloidal form which promotes the hydrolysis. Under the same conditions an unseeded solution of identical composition yields only 30 to 70 per cent of its titanium content.

Such nuclei were prepared by treating a titanium sulfate solution, such as that used for hydrolysis, with sodium hydroxide until neutral to methyl orange or bromophenol blue, and heating the resultant suspension of titanium oxide in a sodium sulfate solution at 100° C. for 5 minutes. If the cured product was not to be used immediately, it was cooled at once to 60° C. or below, for within this temperature range the nucleating property did not deteriorate significantly for several weeks. The hydrous titanic oxide of the cured suspension was the active nucleating agent, and a more concentrated seed was obtained by allowing the product to settle and then decanting part of the supernatant liquor. As an example, a small part of an ilmenite liquor containing 185 g. to 213 g. titanium dioxide and 440 g. to 502 g. potential sulfuric acid per liter was neutralized at 74° to 80° C. with aqueous sodium hydroxide employing methyl orange as indicator, and held at 80° to 100° C. for 15 to 30 minutes to develop the nucleating property to the maximum degree. This cured suspension was then added to the remainder of the original solution, and the mixture was heated just below the boiling point, 100° to 105° C., until hydrolysis was complete.

According to another modification, hydrolysis of concentrated solutions at atmospheric pressure was promoted and hastened by the addition of a small proportion of hydrous titanium oxide, still capable of homogeneous dispersion, which served as accumulation centers for the precipitated oxide.[29] Such nucleating suspensions were prepared by adding a portion of the main solution to an aqueous alkali to bring the pH to 4.0 to 4.5 and heating at 70° to 80° C. for 15 to 30 minutes. Unless used immediately, the nuclei were cooled rapidly to below 60° C., for if held at 80° C. they became overripe and lost activity. Ilmenite solutions seeded with 1 per cent of such agents, based on the titanium dioxide, gave a yield of 95 per cent after boiling for 2 to 3 hours at atmospheric pressure.

The chemical and physical properties of hydrous titanium oxide produced by the thermal decomposition of sulfate solutions varied according to the conditions under which the precipitation was carried out. A product which yielded pigment of good quality was obtained by carrying out the hydrolysis in the presence of added colloidal titanium dioxide prepared by adding a concentrated sulfate solution to a greater quantity of boiling water at a constant rate in 4 to 6

minutes. Regular nonseeded ilmenite solution diluted to 160 g. titanium dioxide and 400 g. potential sulfuric acid per liter to correspond to the concentration of a nucleated charge yielded only about 30 per cent of its titanium content after heating at 100° C. for 24 hours. After adding colloidal titanium oxide nuclei to another portion of the solution, however, a 95 per cent yield was obtained in 3 hours under the same conditions.

Such nucleating agents were prepared by adding at a constant rate with agitation to a larger volume of boiling water, over a period of 4 to 6 minutes, an ilmenite liquor containing 200 g. titanium dioxide and 500 g. sulfuric acid per liter, free and combined with titanium. As the two solutions were mixed, colloidal titanium dioxide formed immediately and continued to increase in amount, after the mixing was completed, to a maximum value. After a short time, however, precipitation began, and the concentration of the colloid therefore decreased. The colloidal component may be determined quantitatively by passing a sample of the liquor through a filter medium to remove any precipitated oxide, treating the filtrate with an equal volume of concentrated hydrochloric acid, and boiling to effect complete coagulation. The coagulated material was then filtered, washed, dried, and weighed. As soon as the colloid phase reached a maximum value, the dispersion was stabilized by cooling rapidly to below 60° C. In this condition it remained active for some time.

Such a nucleating agent was mixed with an ilmenite solution containing 200 g. titanium dioxide and 500 g. potential sulfuric acid per liter in such proportions that the content of active acid of the seeded mixture was 400 g. per liter. Hydrolysis was carried out by heating the mixture at the boiling point for 3 hours. Proportions of colloidal titanium compounds in the solution to be hydrolyzed may be varied within wide limits. A great improvement in yield was noted with a concentration as low as 1.5 g. to 2.0 g. per liter, and values up to 30 g. per liter were used. The final acidity of the hydrolysis liquor was also important, and values of 400 g. per liter were employed, since maximum recovery of titanium was obtained up to approximately this concentration. Although lower strengths gave good yields of titanium, the recovery of waste acid from the dilute liquors was not economical. The presence of iron in the solution to be hydrolyzed did not interfere with the reaction, but if the proportion was excessive it was reduced by crystallization as ferrous sulfate.[30]

Dahlstrom and Ryan [31] found that the precipitate obtained from titanic sulfate solutions poor in acid functioned as seeding agents for

ilmenite liquors of usual concentrations, greatly increased the colloidal phase, and shortened the initial period before precipitation was evident. Furthermore the total time of hydrolysis was shortened appreciably and the product was of improved quality. In preparing nuclei of this type, a solution of titanium sulfate was partially neutralized with sodium hydroxide or other alkali to a pH between 1 and 2, and stirred until all turbidity disappeared. The clear product was then diluted to the desired concentration and heat-treated to develop the nucleating property to the maximum degree.

Alternatively, orthotitanic acid was dissolved in 1 to 5 per cent aqueous sulfuric acid containing sodium sulfate, magnesium sulfate, sodium nitrate, or a similar salt. These compounds apparently facilitated dissolution of the orthotitanic acid by forming complex compounds. As before, the liquor was heated to precipitate the nucleating agent. In both cases the hydrous titanium oxide nuclei were not true colloids but a definite microscopic precipitate which remained as such after mixing with the ilmenite solution and heating to boiling. The acidity at which these seed were prepared was important, and values corresponding to a pH of 1 to 2 were found to give best results. Precipitation of effective nuclei was also a function of both temperature and time of curing; the higher the temperature the shorter the time. The most desirable range was found to be between 60° and 100° C., and heating was continued until 85 to 95 per cent of the total titanium had been precipitated. This required from 10 minutes to 4 hours.

The properly cured nuclei were added to regular sulfuric acid solution of ilmenite, and the charge was heated at or near the boiling point until the desired yield of hydrous titanium oxide was obtained. The precipitate was then processed in the usual manner to produce a pigment of high quality. Such nuclei were effective at both high and low acid concentrations, and in both "acid" and "basic" titanium sulfate solutions, that is, containing more or less active sulfuric acid than that corresponding to the normal salt. The proportion of the liquor used for preparation of the seeding agent was as high as 15 per cent of the total to be hydrolyzed, but in general 1 per cent proved effective.

In an example, an ilmenite solution containing 6.4 per cent titanium dioxide, 20.6 per cent potential sulfuric acid, free and combined with titanium, and 6 per cent ferrous oxide was employed. Of the titanium, 0.02 pound per gallon calculated as the dioxide was in the trivalent state. To 123 pounds or 15 per cent of this solution, 13.7 pounds of sodium carbonate, equivalent to one half of the active acid,

was added with constant agitation, and the product was diluted with 60 gallons of water to reduce the acidity to 2.5 per cent. Turbidity which developed initially disappeared on stirring, and the clear product was heated at 100° C. for 20 minutes to precipitate the desired nuclei. After cooling and settling, the supernatant liquor was removed by decantation and the precipitate was added to the main body of the solution, 697 pounds. The charge was boiled for 11 hours, at which time 95 per cent of the titanium was precipitated as hydrous oxide. In another case an ilmenite liquor from which part of the iron had been removed by crystallization as ferrous sulfate was employed. Analysis showed 12.9 per cent titanium dioxide, 3.5 per cent ferrous oxide, and 21.6 per cent potential sulfuric acid. As before, 0.02 pound per gallon of titanium expressed as the dioxide was in the trivalent state. Alternatively, orthotitanic acid precipitated by adding 1.44 pounds of sodium hydroxide dissolved in 10 gallons of water to 8.15 pounds of the above liquor was filtered and washed, and redissolved in an aqueous solution of 0.4 pound sulfuric acid and 2.3 pounds sodium sulfate. The final weight was 26.2 pounds. It analyzed 4 per cent titanium dioxide, 9 per cent sodium sulfate, and 1.6 per cent sulfuric acid, and had a hydrogen ion concentration corresponding to a pH of 1.5. This orthotitanic acid solution was then heated to 85° C. and held at this temperature for 90 minutes. At the end of this period about 95 per cent of the titanium had been precipitated in a form suitable for use as nuclei. This product suspended in the mother liquor was added to 407 pounds of the original crystallized ilmenite solution and the seeded mixture was boiled for 2 hours. The precipitate of hydrous titanium oxide, which represented a recovery of 95 per cent, was filtered, washed, and calcined in the usual manner.

According to a related method,[32] a sulfate solution of ilmenite was first freed from iron and then neutralized with aqueous ammonia. The precipitate formed was redissolved by agitation in the presence of ammonium chloride, and the system was heated to develop the nucleating property to the maximum degree. From 0.5 to 10 per cent of this seeding material was added to regular ilmenite solution to initiate and assist hydrolysis.

Titanium oxide precipitated by thermal hydrolysis from solutions containing considerably less sulfuric acid than that corresponding to the titanyl salt was observed to possess high nucleating power.[33] Such solutions were prepared by dissolving orthotitanic acid in titanyl sulfate solution or by neutralizing part of the active acid with sodium hydroxide or other alkali, although the latter method gave

better results. The pH values were maintained below 2. A regular ilmenite solution containing from 100 to 140 g. titanium dioxide, 200 g. to 700 g. sulfuric acid, and 50 g. to 90 g. ferrous iron per liter was treated at room temperature with a base such as sodium hydroxide or ammonium hydroxide in such quantity that titanium hydroxide precipitated, but completely redissolved in a comparatively short time at 20° to 30° C. The liquor was then adjusted to a concentration of 30 g. to 60 g. titanic oxide and 10 g. to 30 g. active sulfuric acid per liter, and heated at 80° C. to precipitate the active nuclei. Regular ilmenite solution was seeded with 1 to 6 per cent of this cured suspension, calculated on the titanium dioxide, and boiled for 1 to 3 hours until 95 to 97 per cent of the titanium had been thrown down. The precipitate was filtered, washed, and calcined according to conventional methods to develop optimum pigment properties.

In an example, 4 per cent of an ilmenite solution containing 80 g. titanium dioxide, 253 g. sulfuric acid, and 85 g. iron per liter, and having a specific gravity of 1.43, was removed from the main batch, mixed with dilute sodium hydroxide to bring the titanium dioxide and sulfuric acid to 40 g. and 15 g. per liter, respectively. A turbidity appeared initially but vanished completely on stirring for 1 or 2 hours. This strongly basic solution was heated at 80° C. for 2 hours to develop the nucleating property to the maximum degree and then added to the remaining 96 per cent of the original ilmenite liquor. The seeded mixture was boiled to precipitate the titanium component as hydrous oxide. A recovery of 96 per cent was obtained in 2.5 to 3 hours. The precipitate was washed, dried, and calcined to produce a pigment of good color and high tinting strength.

Schmidt [34] prepared a seeding material by heating at 70° C. the product obtained by neutralizing iron-free titanium sulfate solution with sodium hydroxide until a precipitate formed which just redissolved on agitation. The cured nuclei were added to regular ilmenite solution, and the mixture was heated to effect hydrolytic precipitation of the hydrous oxide.

Allan and Bousquet [35] found that it was possible to hydrolyze a purified solution obtained directly from ilmenite ore without concentration or removal of iron merely by regulating the sulfate content and adding a suitable seeding agent. By this process titanium dioxide of good pigment properties was obtained from solutions containing as low as 100 g. per liter of this constituent by increasing the amount of stable sulfates. This was accomplished by adding more ferrous sulfate or any other soluble sulfate that would not hydrolyze

along with the titanium, such as that of magnesium, sodium, zinc, or potassium. The factor of acidity was adjusted to 20 to 70 per cent if necessary by adding a basic compound which formed a soluble sulfate. Values between 40 and 50 per cent gave best results. In preparing such solutions ilmenite ore was digested with 2 parts concentrated sulfuric acid and the dry reaction product was dissolved in water or dilute acid. Metallic iron was introduced to reduce the ferric component to the ferrous condition and a small proportion of titanium to the trivalent state. The liquor was clarified by settling after coagulation of the slimes by glue or by filtration after the addition of diatomaceous earth, or a combination of the two, and was not crystallized or concentrated. Analysis showed the following composition:

TABLE 3

COMPOSITION OF HYDROLYSIS SOLUTIONS

Constituent	Grams per Liter
Total titanium dioxide	154
Reduced titanium as dioxide	5
Iron	115
Total sulfuric acid	454
Free sulfuric acid	64
Active sulfuric acid	252

Factor of acidity, 34 per cent. Specific gravity, 1.54.

Active acid equals titanium equivalent sulfuric acid to yield titanyl sulfate plus free acid.

$$\text{Factor of acidity} = \frac{\text{Free acid}}{\text{Titanium equivalent sulfuric acid}} \times 100$$

Titania gel corresponding to 2 per cent of the titanium content was added to the solution and the mixture was boiled for 5 or 6 hours to effect a 95 per cent recovery. The precipitate was filtered, washed, and calcined in the usual manner.

Other types of nuclei, such as colloidal titanic oxide formed in place, may be used. If it was desired to employ solutions of lower titanium content, additions of a soluble salt such as magnesium or ferrous sulfate were made to increase the total concentration, which was the important factor. The properties of the pigment obtained were improved for any given titanium concentration by increasing the concentration of soluble sulfates in the hydrolysis solution, and by-product ferrous sulfate was effective. The process permitted further economies in that titanium solution containing an extremely low free acid concentration could be employed.

Products of improved pigment properties were obtained from solutions containing high percentages of titanium, though poor in acid, by adding small amounts (0.05 to 5 per cent based on titanium dioxide) of alkali silicates, or oxides, hydroxides, or carbonates of zinc, magnesium, the alkali metal, or ammonia prior to or during the hydrolysis step.[36] The small proportion of alkaline agent introduced did not cause any appreciable decrease in the total acidity of the system but rather acted as initiator of the reaction. Acid-poor ilmenite liquors of this type were in a metastable condition, and the alkali broke down the metastability and started hydrolysis by a sudden local decrease in acidity. The initial solutions contained from 150 to 250 g. titanium dioxide per liter, and up to 50 per cent less sulfuric acid bound to titanium than that required to form the normal salt. All the iron component was reduced to the ferrous state and a part was removed by crystallization as copperas. In some instances further purification was effected by treatment with hydrogen sulfide and the liquor was clarified. From 1 to 10 kg. of the alkaline material (sodium carbonate) per cubic meter of solution was very effective, although as low as 0.1 kg. gave noticeable improvement. The upper limit was a proportion equivalent to 10 per cent of the acid combined with titanium. Hydrolysis was readily effected by boiling the seeded liquor in an open vessel. The reaction proceeded more rapidly, however, at autoclave pressure. Heat was applied indirectly through steam coils or by injecting live steam. After hydrolysis had proceeded to completion, the precipitate was washed, treated, and calcined at 900° to 1000° C. to obtain a pigment of higher tinting strength. A typical solution contained 200 g. titanium dioxide per liter and enough sulfuric acid to combine with the iron and other bases, and an additional quantity of acid, 20 per cent less than that theoretically required to combine with the titanium present to form the normal salt.

Hydrolysis was further accelerated by adding an alkaline compound such as sodium carbonate or calcium hydroxide in the dry form to boiling titanium sulfate solution.[37] The results were a function of the ability of the dry material to react locally with the ilmenite solution to produce a change in the physical conditions of the titanium compounds present. It was the production of a particular colloidal state of titanic oxide that gave the accelerating effect on the hydrolysis. This was borne out by the fact that dry hydrated lime gave good results, dry calcium oxide was not quite so good, and dry barium or calcium carbonate was only fair. The most soluble and the lowest gravity compounds reacted most rapidly locally and thus

exerted the greatest seeding effect. Distribution of the alkali throughout the solution was avoided. In an example, 2 liters of ilmenite solution containing 202 g. titanium dioxide, 140 g. iron, 630 g. sulfuric acid, 135 g. free acid, 383 g. active acid per liter, and having a factor of acidity of 54.4 per cent, was heated to boiling and 5 g. dry sodium carbonate was added. Boiling was continued, and after 8 hours a yield of 91 per cent was obtained. A solution having a ratio of titanium dioxide to sulfuric acid corresponding to titanyl sulfate has a factor of acidity of zero, and one corresponding to the normal salt has a factor of acidity of 100.

Leuchs [38] treated part of such a solution with a base.as magnesium oxide or sodium hydroxide to precipitate titanium dioxide, and redissolved the separated material in the remainder of the original solution to bring the ratio of titanium dioxide to sulfuric acid to 1. After reduction of the iron to the ferrous state, the solution was heated at 100° C. to effect hydrolysis of the titanium salts. Regular ilmenite liquors were hydrolyzed readily on heating at temperatures above 95° C. after seeding with 1 to 6 per cent, based on titanium dioxide, of a suspension prepared by adding sodium or ammonium hydroxide to a solution containing 30 g. to 60 g. titanium dioxide per liter until the pH was brought to 2, and heating the product at 95° C. to develop the nucleating power to the maximum degree.[39] The partially neutralized solution contained from 2 to 5 moles of titanium dioxide for each mole of sulfuric acid.

Nucleating agents suitable for accelerating the hydrolysis of regular sulfuric acid solutions of ilmenite were prepared by adding an alkaline compound to a portion of the original solution to obtain a low but predetermined acidity, and heating at 75° to 100° C. to develop the desired properties.[40]

From the opposite approach, titanium oxide obtained from hydrolysis of a sulfate solution was treated with a limited amount of sulfuric acid to dissolve the precipitate partially, and the resulting opaque suspension was heated at 80° to 200° C. to develop its nucleating characteristics.[41]

In preparing composite nuclei, an impure titanium sulfate solution was added to an aqueous suspension of a hydroxide or carbonate of an alkaline earth metal in such amount that 96 to 98 per cent of the titanium was precipitated.[42] Under this condition impurities thrown down were redissolved on agitation. The precipitate was washed and the titanium component was redissolved in sulfuric acid to form a strongly basic solution containing the alkaline earth sulfate in suspension. The product was then heated for 1 to 2 hours

at 80° to 90° C. and cooled rapidly to below 60° C. This cured composition was added as a seeding agent in the thermal hydrolysis of ilmenite solutions.

The speed of precipitation of hydrous titanium oxide from sulfate solutions was increased by the presence of a washed oxide from a former hydrolysis.[43] Products obtained in this manner settled rapidly and were readily filtered and washed. The method was applicable to the production of both pure titanium dioxide and composite pigments. In an actual operation, the hydrolysis product of a sulfate solution of ilmenite was washed, filtered, and added to another portion of the original solution in such proportions that the final product was composed of 60 per cent freshly precipitated and 40 per cent of the added compound. The liquor was boiled to effect hydrolysis, and the precipitate was filtered, washed, and calcined.

According to another modification, a pigment containing 25 per cent titanium dioxide and 75 per cent barium sulfate was mixed wet with the solution in such proportions that the final precipitate contained equal parts of the two pigment constituents, and hydrolysis was effected by boiling. The composite precipitate was easily washed and on calcination gave a pigment of high hiding power.

Carpmael[44] added such solutions to a suspension of calcium carbonate in water and agitated the mixture for 6 to 8 hours. The washed precipitate of titanium dioxide and calcium sulfate was made into a paste containing 40 g. to 60 g. titanium dioxide, 15 g. to 30 g. sulfuric acid, and 35 g. to 43 g. sodium sulfate per liter, and heated at 80° to 90° C. for 1 hour to develop the nucleating property. Ilmenite solutions containing iron, vanadium, chromium, and other impurities, after seeding with this material, were readily hydrolyzed on boiling to yield titanium dioxide of pigment quality.

A pure hydrous titanium dioxide which yielded pigment of high covering power was precipitated by thermal hydrolysis from such solutions after nucleating with minute amounts of accelerators obtained by the hydrolysis of titanic and titanyl sulfates in orthotitanic acid solutions.[45]

Better results were obtained by adding seeding materials at intervals[46] during the hydrolysis process. The washed precipitate was treated with potassium carbonate and calcined at 900° C. to develop pigmentary properties.

Allan[47] prepared gelatinous nuclei by treating a solution containing 201 g. titanium dioxide, 437 g. sulfuric acid, and 46 g. iron per liter with aqueous sodium hydroxide (800 g. per liter) in an amount sufficient to react with all potential sulfuric acid except that com-

bined with the iron. During the neutralization the temperature rose to 108° C., and on cooling the mixture set to a solid gel containing 6.6 per cent titanium dioxide. Hydrolysis of regular solutions was readily accomplished by boiling after seeding with approximately 4 g. per liter of this gel. In a typical operation, 1 g. of the dry gel, obtained as described above, was added to 100 ml. of a solution containing 201 g. per liter titanium dioxide, at a factor of acidity of 43, with 46.0 g. of iron per liter, and the mixture was heated to boiling. A 96 per cent recovery was obtained after 2 hours. Nuclear gels of this type were also prepared from other than sulfate solutions, for example chloride, and any alkali or alkaline earth hydroxide or carbonate was satisfactory. Such gels were insoluble in hot and cold water. They could be washed free of soluble salts, although the washed and unwashed gel gave practically the same results. Thermal hydrolysis of ilmenite solutions were also accelerated by an admixture of a gel of titanium dioxide prepared by neutralizing a titanium salt solution with an alkali metal carbonate, and at the same time pigments of better color and brightness resulted.[48] This improvement was attributed to the fact that, employing carbonates as neutralizing agent, gel was produced at a much lower temperature than with caustic alkali. If the temperature rose too high, part of the titanium oxide was converted to a dehydrated form which did not dissolve or disperse in the ilmenite liquor and was carried into and discolored the calcined pigment. To 1 liter of a solution containing 271 g. titanium dioxide, 52 g. ferrous iron, 609 g. total sulfuric acid, 186 g. free sulfuric acid, and 518 g. active sulfuric acid, and having a factor of activity of 56, was added a saturated sodium carbonate solution to neutralize the active acid completely. In this operation the temperature remained at all times below 60° C. This gel was used to seed hydrolysis solutions of compositions similar to that given above.

A composite silica-titania gel produced by intermixing a solution of sodium silicate and a titanium salt showed the same results.[49] Equally effective gels were formed in situ by adding a soluble silicate to the ilmenite solution directly. In either case the mixture was boiled to effect hydrolysis, and the precipitate was washed, dried, and calcined to give a pigment containing a small proportion of silica. Up to 7 per cent, it did not reduce the covering power of the pigment. The value fell off, however, with further addition, but not in proportion to the dilution. In an example, 2000 ml. of a solution containing per liter 191 g. titanium dioxide, 139 g. ferrous iron, 615 g. total sulfuric acid, 136 g. free sulfuric acid, and 370 g. active

sulfuric acid, with a factor of acidity of 58, was added with stirring to 200 ml. of a sodium silicate solution containing 10 per cent silica, and the mixture was boiled for 9 hours to obtain a 91 per cent yield of titanium dioxide. The precipitate was washed, calcined, and milled according to conventional methods.

According to Pollack,[50] titanium dioxide of pigment grade may be obtained by the thermal hydrolysis of sulfate or chloride solutions in the presence of 0.1 to 10 mole per cent of a soluble tin salt or of dispersed hydrated stannic oxide. Alkali metal stannates may be added directly to the main solution. Composites may be obtained by effecting the precipitation in the presence of suspended carriers, e.g., barium sulfate, light spar, or asbestine.

Regular ilmenite solutions were hydrolyzed in a shorter time and at a lower temperature after seeding with a material prepared by taking up the residue obtained on decomposing sodium metatitanate with water in the least quantity of sulfuric acid necessary to give good extraction.[51] In making the nucleating agent, a mixture of rutile and sodium hydroxide was roasted below the melting point and leached to remove the alkali. The washed residue was then extracted with sulfuric acid of 50 per cent strength to yield a solution containing 167 pounds titanium dioxide and 251 pounds sulfuric acid in 100 gallons. One part of this product was added to five parts of the regular ilmenite solution, and the mixture was then heated to bring about hydrolytic precipitation of the titanium.

According to a later development, the titanium oxide concentrate was added directly to the ilmenite solution without being previously dissolved in sulfuric acid.[52] Rutile was heated with sodium hydroxide and the reaction product was washed with water or dilute acid to remove the alkali remaining. This residue was added to regular ilmenite solution and the seeded mixture was boiled to effect hydrolysis. Dry powdery sodium titanate, prepared by heating a paste of rutile and concentrated aqueous sodium hydroxide at 500° to 600° C., was found to aid the hydrolytic decomposition of such solutions.[53] For example, a mixture of 100 parts rutile, 100 parts sodium hydroxide, and 33 parts water was kneaded, dried, and heated at 600° to 650° C. for 30 minutes. The reaction product was purified by leaching with dilute sulfuric acid. From 0.05 to 0.20 part of the crude or 0.01 to 0.10 part of the purified product was added to the ilmenite solution for each part of titanium dioxide present. The mixture was boiled to hydrolyze the titanium sulfate and the precipitate was washed and calcined at 800° to 1000° C. to yield pigment.

Active nuclei were obtained by heating a solution or suspension of titanic oxide in the presence of organic acids, e.g., oxalic, tartaric, or salts of these, in proportions sufficient to prevent the formation of particles of more than ultramicroscopic dimensions but insufficient to prevent hydrolysis entirely. These agents served the further purpose of stabilizing the nuclei. It is well known that the hydrolysis of mineral acid solutions of titanium may be inhibited by the addition of organic acids or their salts, e.g., oxalic, citric, and tartaric acids, and sodium citrate. In the presence of appreciable proportions of these agents, very slight or no precipitate forms even on prolonged boiling at relatively high dilutions. In a specific operation, a 2 to 3 per cent sulfate solution of titanium was treated with 3 moles of sodium chloride and one half mole of oxalic acid per mole of titanium dioxide, and then with sodium carbonate until 90 to 95 per cent of the titanium had been precipitated.[54] This product was washed and boiled with water to give a colloidal solution for use as seed.

According to Cauwenberg,[55] the hydrolysis of titanium sulfate solutions may be initiated and maintained by the addition of organic compounds which liberate ammonia (hexamethylene tetramine, acetaldehyde ammonia, and acetamide) before or during hydrolysis. Alternatively, a small part of the solution may be activated by boiling with such agents, and then returned to the main body, whereby the dispersed particles of titanium compounds act as nuclei for further precipitation. Best results were obtained by adding the seed to the ilmenite solution at 85° C. and raising the temperature to boiling within a short time.

By precipitating titanium hydroxide from sulfate solutions in the presence of a finely dispersed salt of titanium soluble in dilute mineral acids, a finely divided product of pigment grade was obtained.[56] Such compounds are titanium phosphate, the double sulfate of titanium and potassium, double fluoride of titanium and potassium, silicates of potassium, and salts of titanium and zirconium. These may be formed in solution. One liter of a solution containing 100 g. titanium dioxide, 50 g. iron as ferrous sulfate, and 230 g. sulfuric acid was stirred with 80 ml. of phosphoric acid containing 220 g. phosphorus pentoxide per liter to give a voluminous precipitate which disappeared on stirring for 20 hours. The product, probably a solution of titanium phosphate, gave a fine precipitate of titanium oxide on boiling. Similarly stable titanium hydroxide compounds were obtained by effecting the precipitation in the presence of phosphoric acid or soluble phosphates.[57] After adding a relatively small

proportion of solid basic titanium sulfate to sulfuric acid solutions of ilmenite, hydrolysis was rapidly effected by heating.[58]

Allan[59] reported that in the known processes by which hydrolysis of titanium salt solutions (ilmenite) are initiated or accelerated by seeding agents such as colloidal titanic compounds and calcium sulfate, pigments of improved physical properties were obtained by adding the nucleating agent in a number of portions during the precipitation.

Nuclei Formed in Place

Another advance involves a slow admixture of the ilmenite liquor with hot water or dilute solutions in such a manner that the required nucleating agent is formed in place. Such processes have the advantage of simpler and more rapid operation and lower cost. Furthermore, the hydrolysis is carried out at higher concentrations, thus permitting economical recovery of sulfuric acid from the waste liquor. This method has the added advantage of being particularly applicable to large-scale commercial operation.

Blumenfeld[60] effected the precipitation of hydrous titanic oxide of high purity by bringing together a sulfate solution of ilmenite and hot water, and retarding the rate of mixing so that the resulting liquor first became gradually turbid before the hydrolysis product was precipitated. Hydrolytic decomposition of such solutions by boiling alone gave low yields, particularly if the sulfuric acid content, free and combined with titanium, was as high as 100 g. per liter. The products were filtered with difficulty. Recovery of titanium by hydrolytic decompositions of solutions of this type, as well as properties of the product such as filterability, grain size, and color after calcination, depended not only on the final state of the system but upon certain transformations which the constituents of the solution underwent before and during hydrolysis, and upon the manner in which the final state was arrived at. By this method, however, solutions obtained by dissolving the reaction product produced by heating ilmenite with concentrated sulfuric acid, and containing from 100 g. to 300 g. titanium dioxide per liter, were readily hydrolyzed to yield precipitates having good pigmentary properties. The concentrations of titanium dioxide and sulfuric acid were observed to be the important variables, and the mole ratio should be 1 of the former to from 1 to 2.5 of the latter.

In carrying out the operation, a solution at a temperature above 60° C. was covered with a layer of water in such a proportion as to give, on diffusing or mixing, a liquor of optimum concentration.

Instead of water, dilute solutions of sulfuric or phosphoric acids, aluminum sulfate, or a titanium salt could be employed. Introduction of the second liquor was effected in such a manner that gradual mixing took place. Alternatively, the initial titanium solution was concentrated even to a pasty mass and mixed with a volume of hot water, which was more or less than that removed, so as to bring the concentration of sulfuric acid in the final charge to 300 g. to 367 g. per liter. One of the liquids, usually the more concentrated, was at the time of bringing together at a temperature above 60° C. Mixing was carried out fairly rapidly to avoid appreciable precipitation of hydrous titanium oxide before homogeneity of the liquor had been accomplished and heat had been applied. In both cases the mixture was held at or near the boiling point and the initial volume was maintained. The yield reached 85 to 95 per cent in a few hours in the first method, and in less than 1 hour in the second method. These processes were equally valid for the precipitation of hydrous titanium oxide in the presence of suspended extender materials such as barium sulfate and calcium sulfate.

As an illustration of the method, a solution containing per liter 225 g. titanium dioxide, 50 g. iron, and 440 g. total sulfate, expressed as sulfuric acid, was heated to 95° to 98° C. and covered with a layer of cold water equal to 20 per cent of its volume. This amount of water was sufficient to reduce the total sulfuric acid concentration to 367 g. per liter. After mixing by gentle agitation, the liquor became gradually turbid and precipitated about 94 per cent of its titanium content on boiling for a few hours. According to another modification, a solution containing 180 g. titanium dioxide, 42 g. iron, and 460 g. total sulfuric acid per liter was concentrated to a pasty mass of one half the original volume and introduced into twice its volume of boiling water so that the final concentration was reduced to 300 g. to 310 g. sulfuric acid per liter. Mixing was effected in such a manner as to avoid immediate precipitation.

According to a later improvement,[61] the hydrolysis was carried out in such a manner that an adequate quantity of colloidal titanium oxide was formed in the crystalloid solution prior to any actual precipitation. The exact manner in which the colloidal phase promotes hydrolysis is somewhat controversial, but apparently the titanium in crystalloid solution must pass through the colloid state before precipitation. There is wide variation in the physical and chemical properties of titanium dioxide produced by hydrolysis, dependent upon the exact conditions under which it is carried out,

but by this process titanium dioxide of constantly uniform properties may be produced rapidly and in good yields. At the same time, solutions of high concentration are employed with the result that the sulfuric acid may be economically recovered from the hydrolysis liquor. On the other hand it is not advisable to operate at final acid concentrations much above 400 g. per liter because of the tendency of the stronger solutions to crystallize titanium sulfate initially, and also because of the tendency of hydrous titanium oxide to redissolve in the acid liquor.

In the presence of approximately 30 g. colloidal titanium dioxide per liter, the speed of hydrolysis was increased and a yield of 95 per cent hydrous oxide of improved and uniform quality was obtained on boiling for 3 hours. Iron did not interfere with the reaction, but if much was present in solution it tended to contaminate the precipitate. To overcome this tendency, the iron component was reduced initially to 20 g. to 25 g. per liter by crystallization of ferrous sulfate on cooling.

Solutions of this type, as obtained by the action of sulfuric acid on ilmenite, may vary widely in composition and the ratio of titanium dioxide to sulfuric acid may be designated by "free acidity factor." To illustrate, a solution of free acidity factor of 90, as employed in the examples, contained 90 per cent more sulfuric acid than that required to form titanyl sulfate with the titanium present after the iron had been satisfied. The hydrolysis was carried out with equal success, however, when employing solutions of factor of acidity less than 90 per cent. Much more important than this ratio was total or free acidity of the hydrolyzed liquor. This will be equal to the free acid originally present, plus the acid liberated as a result of the precipitation of titanium dioxide. For practical reasons the final acidity of the hydrolysis liquor was in the neighborhood of 400 g. per liter.

In a specific operation, the solution employed for hydrolysis was prepared by dissolving the reaction product of ilmenite with sulfuric acid in water. Scrap iron was introduced to convert all the ferric component to the ferrous state, and the major portion of the ferrous sulfate was crystallized by cooling and then filtered off. The mother liquor, which contained 190 g. to 210 g. titanium dioxide, 20 g. to 25 g. ferrous iron, and 500 g. to 550 g. active sulfuric acid per liter, was concentrated by vacuum evaporation until sulfuric acid, free and combined with titanium, excluding that combined with iron and other base constituents, was 600 g. per liter. A 100 ml. portion of this concentrated liquor heated to 100° C. was added at

a uniform rate in 4 minutes to 100 ml. of boiling water, with constant stirring. During the first one-fourth minute of the addition a turbidity appeared, but it disappeared almost immediately and the solution regained its original appearance. Temperature was maintained at 103° C., with stirring. After 10 minutes turbidity was again observed, and a few minutes later the suspension assumed a gray color and titanic oxide began precipitating. The reaction was complete in 3 hours, with a recovery of 95 per cent.

The trend of the reaction, as determined by observation and analyses for the first 10 minutes after all the solution had been introduced, is tabulated below. Colloidal titanium oxide in the filtered solution was determined by adding hydrochloric acid to effect coagulation, after which it was readily separated and weighed.

TABLE 4

STATE OF TITANIUM AT DIFFERENT PERIODS OF THE HYDROLYSIS PROCESS

Minutes of Reaction	Appearance of Solution	Constituent (Grams per Liter)		
		TiO_2 in Crystalloid Solution	TiO_2 in Colloid Form	TiO_2 Precipitated
4	Clear	104	21.1	0
5	Clear	97	28.2	0
6	Clear	92	33.0	0
7	Very slight cloudiness	84	40.8	0
8	Very slight cloudiness	78	46.8	0
9	Slightly clouded	70	55.0	0
10	Clouded	71	53.6	0
11	Very clouded	83	41.9	0
12	White	45	31.6	48.2
13	White	43	26.6	55.2

At the beginning of the process, all the titanium was in crystalloid solution. As reaction proceeded, all nonsoluble titanium dioxide was in colloidal form during the initial stages, but as the hydrolysis proceeded further this component increased to a maximum value and dropped off as the amount of precipitation increased.

The reaction occurring during the first few minutes determined the rate and yield of hydrolysis and the quality of the product obtained. At the same time this initial reaction was controlled by regulating the temperature, the speed of mixing, and other variables. At low acid concentrations, such as prevail after only a part of the solution had been added to the water, the tendency to hydrolyze was greatest.

Both the yield of titanium dioxide and the properties of the resulting pigment were affected by the final acidity of the solution, which in turn was a measure of the concentration at which hydrolysis was carried out. This factor may be illustrated by a series of precipitations carried out by adding different volumes of the concentrated solution at a uniform rate to 100 ml. of boiling water, as before. The data are tabulated below.

TABLE 5

INFLUENCE OF FINAL ACIDITY

Test No.	Volume of Solution Added (ml.)	Time of Addition (minutes)	Final Acidity at End of Hydrolysis (g. per liter sulfuric acid)	Time of Analysis after Introduction (hours)	Analysis of Mother Liquor (g.p.l.)			Yield TiO$_2$ (per cent)
					Iron	TiO$_2$	H$_2$SO$_4$	
1	60	2.75	200	1.5	26.3	13.0	215	85.0
2	100	4.0	300	1.5	36.8	19.0	297	84.0
3	200	8.0	380	1.5	42.0	23.2	380	85.0
4	250	10.0	420	2.0	44.2	19.8	410	88.5

TABLE 6

INFLUENCE OF RATE OF MIXING

Test No.	Time of Addition (minutes)	Time of Analysis after Mixing (hours)	Analysis of Mother Liquor (g.p.l.)			Yield of TiO$_2$ (per cent)
			Iron	TiO$_2$	H$_2$SO$_4$	
5	6	2	43.7	76.2	415	57.0
6	10	2	44.2	19.8	408	88.5
7	14	2	44.5	22.6	400	87.0
8	18	2	45.5	26.8	425	85.0
9	26	2	50.8	38.0	418	77.0
10	34	1.75	53.6	110.0	432	35.0 *

* Unfilterable colloids.

Hydrolysis effected at the highest acid concentration not only gave the highest yield, but the resulting pigment had properties superior to those of the other samples.

Development of an adequate colloid phase in the solution prior to precipitation depended in part upon the speed at which the titanium solution was mixed with the water. In the tests shown in

Table 6, 250 ml. of the concentrated solution was added hot, with stirring, to 100 ml. boiling water, as before.

The most favorable results were obtained by introducing the solution of this concentration in from 10 to 18 minutes, that is, at a rate of 4 to 6 minutes per volume of solution added to a unit volume of water. More rapid addition gave poor yields, since an adequate colloid phase was not formed. On the other hand, if introduction
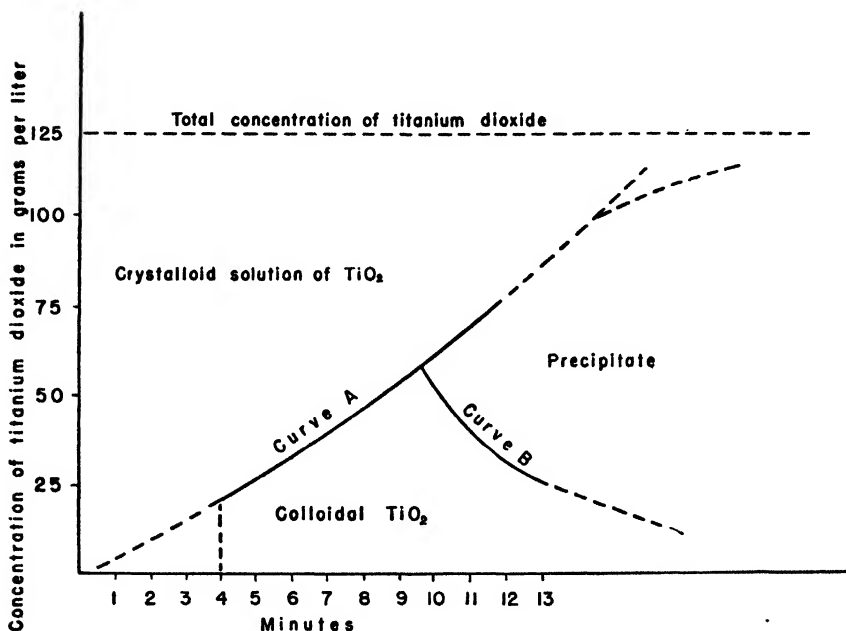
Figure 7. Relationship between concentration of crystalloidal, colloidal, and precipitated titanium dioxide, and time of hydrolysis

was carried out at slower rates, there was a gradual decrease in yield until a considerable precipitation occurred before all the solution had been added. Employing still slower rates, the titanium was not precipitated, but instead it converted to unfilterable colloid form and the yield was very low.

The combined influence of all these factors is shown graphically in Figure 7, in which the concentration of titanium dioxide in the various phases is plotted against the time during hydrolysis. Naturally, the total concentration of the system remains constant. At the initial state of the reaction, all the titanium dioxide was present in crystalloid solution. Curve A shows the progressive increase in the amount not in crystalloid solution. At first all the nonsoluble

titanium dioxide was in colloidal form. When a point is reached, however, at the junction of curves *A* and *B,* the amount of colloid material falls off. Curve *B,* which shows colloidal material alone, indicates the decrease during the rest of the reaction. Obviously the difference between these two curves shows the amount of titanium dioxide precipitated. This figure shows only the first few minutes of the reaction, but as hydrolysis proceeds further, curve *A* rises to approach the total concentration of titanium dioxide present, and curve *B* drops off. Under these conditions, colloidal titanium dioxide was formed immediately on contacting the solution with water, and by the end of the period of introduction this constituent amounted to 20 g. per liter.

In a process employed by Olson,[62] 0.3 to 2.0 per cent of a titanium solution for hydrolysis was added quickly to 20 to 80 times its volume of water. The resulting nuclei were allowed to age and condition for 10 seconds or more, after which the remainder of the original solution was added rapidly and hydrolysis was effected at an elevated temperature.

Hydrous titanic oxide of high purity was precipitated in a very fine state of subdivision by adding a mineral acid solution of titanium to a hot dilute solution containing an organic acid or a salt thereof, such as tannic, tartaric, citric, and oxalic acids, and sodium tartrate and ammonium citrate.[63] Alternatively, the organic compound was added directly to the titanium solution, which was run slowly into hot water with constant agitation to initiate the hydrolysis. Such compounds appeared to have an effect similar to that of the inorganic accelerating agents, calcium sulfate and barium sulfate. Relatively small proportions of the soluble addition agents, much less than required for double decomposition reaction with the titanium salt, were required. More uniform results were obtained by employing hydrolysis solutions prepared from commercial uncalcined titanium dioxide containing only small proportions of impurities.

For example, hydrous titanium oxide was heated with strong sulfuric acid and the reaction product was dissolved in water. All the iron component was reduced to the ferrous constituent, and to prevent reoxidation during processing the reduction was continued until 1 g. per liter titanous ion was formed. Three thousand pounds of such a solution containing 7 per cent titanium dioxide was added to 1500 gallons of a 0.30 per cent solution of oxalic acid at 90° C. during the course of 1 hour. The temperature was maintained constant, and agitation was continued. By the time the components were mixed, 95 per cent of the titanium had precipitated as hydrous

oxide in an extremely fine state of subdivision, but in such a form that it settled and filtered rapidly. The washed product was calcined at 700° to 1000° C.

According to another variation, 32.3 pounds of oxalic acid was dissolved in 3000 pounds of the original sulfate solution containing 7 per cent titanium dioxide, and the product was added to 1500 gallons of water at 90° C. in 1 hour as before. By the time the solutions were thoroughly mixed, 95 per cent of the titanium had been hydrolytically precipitated. The hydrous oxide was filtered, washed, and calcined at 700° to 1000° C. to obtain a pigment having a particle size under 0.89 micron.

According to an improved method applicable in the presence of appreciable proportions of iron, a solution such as was obtained by dissolving the reaction product of ilmenite with sulfuric acid was added to a hot dilute solution containing both an organic acid or an organic acid compound and phosphoric acid or a soluble phosphate.[64] Alternatively, the reagent was dissolved in the titanium-bearing liquor and the product was added slowly to hot water. One per cent oxalic acid and 0.1 per cent phosphoric acid were sufficient to effect hydrolysis. Although iron may be present, it should be reduced to the ferrous state.

In a typical operation, 32.3 pounds of oxalic acid and 2.4 pounds of phosphoric acid were dissolved in 3680 pounds of ilmenite solutions containing 5.71 per cent titanium dioxide, 5.24 per cent ferrous oxide, and 23.81 per cent combined and 2.86 per cent free sulfuric acid, and the combined liquor was added in 1 hour to 300 cubic feet of water at 98° C. Agitation was continuous and the temperature was maintained constant. By the time mixing was complete, 95 per cent of the titanium was thrown down as a fine particle size, easily filtered hydrous oxide. A part of the phosphoric acid combined with titanium and appeared in the precipitate. The product was washed and calcined at 700° to 1000° C. to yield titanium dioxide of high purity having good pigment properties.

Hydrolysis was effected by adding the titanium-bearing solution to boiling water carrying in suspension a small proportion of colloidal material, specifically silicic acid, capable of bringing the hydrous titanium dioxide to a physical state in which it was readily filtered and in which it possessed the final quality of pigment.[65] If ilmenite solutions were used, reduction was carried to the point that 5 per cent of the titanium was converted to the trivalent form and a part of the ferrous sulfate was removed by crystallization on cooling. Composites were similarly produced by

effecting precipitation in the presence of fillers, such as barium sulfate, either added to or formed within the solution. The product was filtered, washed, treated with a borate, and calcined.

Thermal hydrolysis of ilmenite solutions to produce an oxide free from iron was accomplished by adding the solution slowly to an aqueous and approximately neutral dispersion at 90° C. of a protective colloid such as dextrin and a salt which was relatively insoluble in water but completely soluble in the sulfuric acid liquor produced during the process.[66] Salts of this type include the fluorides and oxalates of tin, antimony, titanium, thorium, aluminum, germanium, zinc, and zirconium. According to this process, hydrolysis of concentrated titanium sulfate solutions was readily accomplished with very slight dilution of the original solution. The temporarily insoluble salt initiated the first stages of crystallization and thus formed the seed. Later the salt dissolved in the hydrolysis liquor. The function of the protective colloid was to prevent the aggregation of the seed particles of titanium dioxide already initiated by the temporarily insoluble salt, and it also acted in an auxiliary manner by furthering the maintenance in solution of the iron salts.

In an example, 200 ml. of clarified and crystallized sulfate solution of ilmenite, having a specific gravity of 1.35 and containing 7.5 per cent titanium dioxide and 20 per cent sulfuric acid free and combined, was added at 30° to 80° C. at a uniform rate in 15 minutes to 250 ml. of a solution containing 0.3 per cent dextrin and 0.4 per cent suspended aluminum oxalate at 90° C. Hydrolysis resulting from the mixing of these solutions produced a large number of hydrous titanic oxide particles to serve as seed, and 800 ml. of the original ilmenite solution was added very quickly. The system was raised rapidly to 98° C. and maintained at this temperature, with agitation, for 30 minutes, until the dextrin was converted to soluble sugar. This resulted in complete hydrolysis of the titanium sulfate and the precipitate was washed and calcined by conventional methods.

According to a modified procedure,[67] solutions of the same type were diluted with water containing 0.5 per cent of a colloidal polysaccharide (dextrin) and boiled to effect hydrolysis. At the same time the dextrin was converted to sugar.

Two volumes of a 10 to 20 per cent solution of titanium sulfate, and 2 volumes of a 0.75 per cent solution of dextrin, both at 80° C., were added simultaneously at a constant rate to 1 volume of water at 90° C., and the mixture was boiled to complete the hydrolysis.

Ilmenite solutions containing 0.5 to 2 per cent antimony trioxide based on the titanium dioxide were hydrolyzed directly by boiling under atmospheric conditions, without seeding, to produce pigment of high quality possessing strong resistance to chalking.[68]

To improve the filtering and washing rate [69] of the hydrolysis product, 10 per cent of a sulfuric acid solution of ilmenite was set aside and the remainder, heated to 90° to 100° C., was added in 15 minutes, with constant agitation, to one fifth its volume of water or dilute acid at the same temperature. After boiling for 0.5 to 2.0 hours, the remaining 10 per cent of the solution was added, and heating was continued for 3 to 4 hours to complete hydrolysis. Wood [70] found that the filtration rate of the precipitate, as well as the ultimate pigment properties, could be improved by greatly reducing or stopping altogether the normal agitation of the liquor during the portion of the hydrolysis period that transition of the solution from a true colloid to a suspension of filterable particles is taking place. Hydrolysis was initiated by adding a relatively concentrated titanium solution to water maintained at an elevated temperature, whereby a relatively large number of nuclei were formed. Constant agitation was maintained during and after mixing until flocculation or coagulation of the hydrolyzing particles took place. The system was then allowed to stand undisturbed until it presented a cream-colored appearance, to indicate the presence of white titanic oxide flocculated into particles of the desired filterable dimensions. At this stage agitation was resumed and maintained until hydrolysis was complete. At the end of the mixing operation, the liquor appeared relatively clear, but within a few minutes a slight turbidity developed and the colloidal solution passed from black to olive green to steel gray. As this change became more rapid, agitation was suspended. The color changed rapidly through tan to the indicative cream shade. This step increased the filter rate by 50 per cent and was particularly applicable to the Blumenfeld type of hydrolysis.

In an example, 3 volumes of ilmenite solution containing the equivalent of 200 g. titanium dioxide, 25 g. iron as ferrous sulfate, and 600 g. sulfuric acid per liter, at 100° C., was added slowly to one volume of boiling water with constant agitation. During mixing a precipitate formed, but on further addition of the solution it became dispersed so that at the end of the introduction period the solution appeared relatively clear. A few minutes after the last of the liquor had been added, a slight turbidity appeared and became more marked as the color of the colloidal solution passed succes-

sively from black to olive green to steel gray. As the color change became more rapid, agitation of the liquor was stopped entirely for a period of 10 minutes, during which time the color of the mixture changed rapidly through tan to cream. During this period the system changed from a true colloidal suspension to a suspension of flocculated titanium dioxide of filterable size. At this stage the agitation was resumed and the solution was boiled for 3 hours to complete hydrolysis.

Constant Composition During Hydrolysis

Farup [71] found that by effecting thermal hydrolysis in a solution of approximately constant composition, a precipitate of greater uniformity and of optimum properties was obtained. The composition, purity, and physical properties of hydrolytically precipitated titanium dioxide depend to a great extent upon the conditions under which the decomposition takes place, such as composition of the solution employed, temperature, and duration of boiling. In the commonly employed processes, great changes in the concentration of the solution take place as the precipitate is formed and an equivalent amount of acid is liberated. Thus the formation of titanic acid will take place under entirely different conditions at the beginning and at the end of the operation.

To overcome this effect, a titanium-rich solution, 50 g. to 300 g. titanium dioxide per liter as prepared from ilmenite, was led into a precipitation vessel and heated until practically complete hydrolysis had taken place. Four fifths of the liquor was then removed. To the remaining one fifth at precipitation temperature, fresh solution was added at such a rate as to secure a practically constant content of dissolved titanium until the vessel was filled. Heating was continued throughout the process. The supply of solution was then interrupted, and four fifths of the liquor was again removed. The operation was repeated as often as was desired. A typical solution contained 9.1 per cent titanium dioxide, 10.9 per cent ferrous oxide, 30.2 per cent sulfur trioxide, and trivalent titanium equivalent to 1.5 g. per liter of the dioxide. After hydrolysis had been carried to the desired stage, the product was filtered and washed.

The ilmenite solution was also added continuously to the hot mother liquor at such a rate that the composition of the solution remained constant as the titanium salts gradually hydrolyzed.

According to Saklatwalla, Dunn, and Marshall,[72] thermal hydrolysis carried out in the usual manner tends to start out at a

very rapid rate which gradually falls off as the reaction proceeds so that the initially precipitated titanic oxide not only occludes more metallic impurities than that thrown down later at a slower rate but has a somewhat larger particle size. This fraction, constituting 20 to 30 per cent of the total, contaminates the entire precipitate so that the resulting pigment does not have the optimum color and tinting strength. However, by increasing the free acid content of the solution to 6 to 14 per cent, the initial rate of hydrolysis was slowed down, with the result that the quality of the first portion precipitated was greatly improved in properties. To illustrate, the reaction product of ilmenite with concentrated sulfuric acid was leached with water to extract the soluble titanium and iron sulfates. The solution containing 6 to 8 per cent titanium dioxide was treated with metallic iron to reduce the ferric component to the ferrous state, filtered, and cooled to crystallize part of the ferrous sulfate. After adjusting the free acid content to 10 per cent, the solution was heated to 180° to 190° F. and diluted with 10 per cent sulfuric acid at 200° F. to reduce the titanium dioxide content to 2 to 4 per cent. The adjusted solution was further heated to effect hydrolytic precipitation of the titanium. Because of the excess acid, the reaction proceeded at a much more uniform rate, and the initial fraction of poor quality which would have occurred without the excess acid was avoided. The product was washed, dried, and calcined according to conventional practice. Instead of adding acid to the solution, the proper excess was acquired by increasing the ratio of sulfuric acid to ore in the digestion step.

Titanic oxide of improved color was obtained by carrying out the thermal hydrolysis of sulfate solutions in the presence of hydrofluoric acid or a fluoride salt.[73] The clarified solution was boiled to effect hydrolytic precipitation, and water was added as the reaction proceeded to reduce the concentration of free acid and increase the yield of titanium. Pigments produced in this manner were free from iron and had a more granular structure. The decomposition of titaniferous ores and the thermal hydrolysis of the resulting solution were reported to be facilitated by adding a small proportion of calcium fluoride to the sulfuric acid used in the digestion stage.[74]

Titanic oxide obtained by hydrolyzing an ilmenite solution in the presence of reducing compounds, such as sodium sulfite, in a proportion equivalent to the ferric iron and other oxidizing agents present, did not discolor on heating to incandescence.[75] The color was also improved by digesting the hydrolysis product in the mother

liquor under pressure at 135° to 140° C.,[76] and by a second dissolution and hydrolytic precipitation of the hydrous oxide obtained initially from ilmenite solution.[77]

Yields from the thermal hydrolysis of sulfate solutions of titanium may be increased by adding water during the process.[78] By the usual methods involving boiling at atmospheric pressure, 90 to 93 per cent recovery is obtained in a few hours, and prolonged heating causes practically no further precipitation. The addition of water after most of the titanium sulfate has been hydrolyzed produces a sudden decrease in concentration, with a consequent acceleration of hydrolytic decomposition, so that the reaction proceeds to completion in a comparatively short time. There is some tendency at this stage to precipitate titanium oxide in a finely divided form which occludes iron compounds, but this may be effectively overcome by discontinuing the heating while the water is being added. The procedure is applicable to the production of both the relatively pure oxide and composite pigment.

For example, an ilmenite solution having less sulfuric acid than that required to form normal sulfates was reduced, clarified, filtered, and cooled to crystallize ferrous sulfate, and the mother liquor was then concentrated by vacuum evaporation. Fifteen cubic meters of this solution, containing 215 g. titanium dioxide, 345 g. sulfuric acid, and 80 g. ferrous iron per liter was boiled for 4 hours. The steam was then shut off and 1.8 cubic meters of water was added, with stirring. Heat was again supplied, and after boiling for 1 hour more the recovery was 97 per cent. In another operation, to 30 cubic meters of an ilmenite solution of specific gravity 1.44, containing 90 g. titanium dioxide and 260 g. sulfuric acid per liter, barium sulfate was added in a proportion calculated to give a product containing 25 per cent titanium dioxide, and the suspension was heated by injecting live steam. After boiling for 3 hours, 80 per cent of the titanium precipitated. At this stage the steam was cut off and 5 cubic meters of water was added, with stirring, causing the temperature to drop to 93° C. The system was again heated to boiling, and in 2 hours more than 98 per cent of the titanium was recovered. The water was added continuously to the hydrolysis mixture at such a rate as to maintain the concentration of sulfuric acid at a constant value approximately equal to that of the liquor just before precipitation began.

As already indicated, the hydrolysis of ilmenite solution is effected generally in the presence of a small proportion of titanous salt to hold the iron component in the stable ferrous condition.

Trivalent titanium does not precipitate on boiling the solution, and, to increase the final yield, near the end of the process this component may be oxidized to the readily hydrolyzed tetravalent form by adding ferric oxide to the acid liquor.[79]

Continuous Process of Hydrolysis

Saklatwalla and Dunn [80] developed an interesting process for the continuous hydrolysis of dilute titanium sulfate solution. In order to secure optimum conditions for hydrolysis, the solution was very quickly raised to the proper temperature, maintained for the exact period of time required for effecting the desired degree of precipitation and no longer, and then cooled to arrest further reaction. These conditions were readily attained by passing the solution continuously through a long hydrolyzing tube of any convenient length, depending primarily upon the velocity of flow, which, however, was sufficient to secure efficient heat transfer from the walls to the solution and to carry along the precipitated hydrous titanium dioxide. Such a reaction chamber consisted of a lead-lined pipe 1 inch in diameter with a total length of 1000 to 1500 feet.

The method was particularly applicable to ilmenite solutions containing approximately 4 per cent titanium dioxide and 6 to 10 per cent sulfuric acid in excess of that required to form normal salts with the titanium and ferrous iron present. In actual operation such a solution was supplied at room temperature and at a pressure of 35 to 45 pounds per square inch to the inlet end of the hydrolyzer, and steam, also at 35 to 45 pounds pressure, was introduced at the same end around the tube. The parallel flow provided for a maximum heat transfer at the inlet end of the tube so as to bring the solution very rapidly to the decomposition temperature, 255° to 265° F. Once attained, this temperature was maintained throughout the length of the hydrolyzer. Thus each small incremental volume of solution was immediately subjected to the maximum heating effect of the steam and was very quickly brought to the temperature required for hydrolysis. Also the velocity of flow of the solution and steam through the system favored rapid heat transfer through the walls of the tube. The time of reaction was so regulated that 85 to 90 per cent of the titanium dioxide was precipitated, since this was found to be the maximum recovery consistent with high quality of the product. One half hour was required for any one portion of the solution to travel through the hydrolyzer. The reaction product was immediately cooled on discharging so as

to check any further hydrolysis, and particularly to avoid colloidal material which tended to form on slow cooling. As in other methods of procedure, the hydrous titanium dioxide was filtered, washed, and calcined.

Because of such accurately controlled conditions, the time of precipitation was shortened appreciably over that of the batch process. Although the method was applicable to various types of solutions, sufficient free sulfuric acid was present to prevent an undesirable initial precipitation of basic sulfate and to cause the hydrolysis to proceed from the start at a slower rate.

Studies of Methods of Hydrolysis

In a study of the commercial methods employed in producing titanium dioxide pigments of the anatase type, Pamfilov, Ivancheva, and Soboleva [81] compared the Mecklenburg process, in which nuclei are prepared separately and added to the solution for hydrolysis, with the method developed by Blumenfeld in which the seeding agents are formed in place within the main body of the hydrolysis solution, from the point of view of adaptability, yield, and quality of the products obtained. These two processes were selected for investigation because of their paramount practical importance and wide commercial use. Solutions employed in the greater part of the work were prepared on a laboratory scale by dissolving the reaction product of titanomagnetite concentrate with strong sulfuric acid, although some were obtained from the Leningrad plant. The concentration of titanium dioxide ranged from 120 g. to 250 g. per liter, and the iron, after reduction to the divalent condition, was brought to 25 g. to 30 g. per liter by crystallization, as ferrous sulfate on chilling. Precipitations were carried out as nearly like plant conditions as possible. Descriptions of the methods employed are given below in detail.

MECKLENBURG. Clarified, reduced, and crystallized sulfate solutions containing 120 g. to 150 g. titanium dioxide and 25 g. to 30 g. per liter iron in the divalent state were used. In preparing the nuclei, 5 per cent of this solution was made neutral to methyl orange at 80° to 85° C. by adding 20 per cent aqueous sodium hydroxide. The grayish suspension obtained was held at 80° to 85° C. for 15 minutes to develop the nucleating properties to the maximum degree, and then added to the other 95 per cent of the original solution. The seeded mixture was heated at 102° to 106° C. for 5 hours to complete hydrolysis, and cooled to room temperature. Turbidity

was quite noticeable after 20 minutes heating. Increase in the proportion of nuclei above 5 per cent did not increase the yield appreciably, but on the other hand gave a product of poor color. The precipitate of hydrous titanium oxide was filtered, washed, dried at 100° C., and calcined at 800° to 1000° C. for 2 hours to develop the optimum pigment properties.

BLUMENFELD. Reduced and crystallized solutions, as used before, were concentrated by vacuum evaporation to 200 g. to 270 g. per liter titanium dioxide. The acid factor, that is the ratio of active sulfuric acid (free and combined with titanium) to the titanium dioxide, was varied over fairly wide limits. A portion of the solution to be hydrolyzed, maintained at 94° to 96° C., was poured at a uniform rate in 16 minutes into one third its volume of water, initially at 91° C. Heat was applied so that at the end of this period the temperature of the system was 102° C. The mixture was then heated slowly to the boiling point and boiled for 5 hours. A marked precipitation occurred after 45 to 50 minutes. The hydrous titanium oxide obtained was washed, dried, and calcined as before.

Results obtained showed that, at a constant concentration of titanium dioxide in the solution, an increase in acid factor, ratio of active sulfuric acid to titanium dioxide by weight, decreased the yield. This was especially noticeable in the Blumenfeld method. Increasing the acidity of the solution and decreasing the concentration of titanium resulted in pigments of lower tinting strength. In the Mecklenburg process, employing solutions of a constant acid factor, the yield increased as the concentration of titanium decreased, but this trend was not distinct in the Blumenfeld process. The Mecklenburg method, even at acid factors greater than 4, gave yields of 96 per cent, while that of Blumenfeld gave good yields with acid factors not greater than 2.7, though best results were obtained at about 2. Color, brightness, and other physical properties were better in this process.

Solutions of low acid factor but of high active acid content gave lower yields. Active acid was seldom higher than 35 per cent. By following the conditions normally employed in the Blumenfeld method of hydrolysis, good results were obtained using solutions of much lower concentration than those commonly recommended.

Work, Tuwiner, and Gloster [82] studied the hydrolysis of sulfate solutions having titanium dioxide concentrations of 1.54 to 8.97 per cent and ratios of sulfur trioxide to titanium dioxide from 1.61 to 3.75. Pigments of greater covering power were obtained at the higher concentrations of titanium and the lower acid ratio, although

all unseeded solutions gave products inferior to the best commercially available pigment. The concentration of the mother liquor, after hydrolysis was complete, was found to have an important influence on the properties of the precipitate. Similar solutions [83] having ratios of titanium dioxide to sulfur dioxide between 1.0 to 1.66 and 1.0 to 0.65, and a commercial sample of ratio 1.0 to 2.26 hydrolyzed by refluxing without previous nucleation, gave products of low hiding power and poor color. However, after seeding, those liquors having ratios between 1 to 1 and 1.0 to 1.65 yielded pigments of high opacity as measured by turbidity of aqueous suspensions. Solutions more basic than 1 to 1 were autoseeded on dilution with water to an opalescence approaching turbidity, and acted accordingly on refluxing. Hixon and Plechner [84] prepared solutions of various concentrations and acidities by dissolving crystalline titanyl sulfate, $TiOSO_4 \cdot 2H_2O$, in dilute sulfuric acid, and effected hydrolysis by boiling under reflux. With increasing concentrations the proportion of hydrous titanic oxide precipitated in a given time decreased to a minimum value, then increased to a maximum and again fell off. Braun [85] found that the hydrolytic precipitation of titanic oxide from sulfate solutions was influenced by concentration, temperature, hydrogen ion concentration, manner of agitation, and presence of foreign substances both organic and inorganic.

Solutions obtained by dissolving the product formed by treating ilmenite or metatitanic acid in 70 per cent sulfuric acid at 120° C., and then at 140° to 160° C. for 1.5 hours, showed no change of viscosity or composition after 6 months.[86] Very active seeding agents obtained by heat-treating a solution containing 50 g. titanium dioxide and 16 g. active sulfuric acid per liter had a deep brown color and blue opalescence but was transparent in transmitted light. Ilmenite solutions containing 110 g. titanium dioxide and 220 g. active sulfuric acid per liter, after inoculation with 1 per cent of this nucleating suspension, gave a 95 to 98 per cent recovery in 1 hour. Hydrolysis started at 96° C. and was completed at 102° C. Such nuclei were more effective than the product produced by Mecklenburg.

A study of thermal hydrolysis of pure $TiOSO_4$ solutions showed that half the sulfuric acid split off rapidly and that after this the rate of hydrolysis was very slow.[87]

From studies of an analytical procedure, Kayser [88] noted that complete hydrolysis of titanium sulfate solutions took place at pH of 6.5, although other workers precipitated hydrous oxide of optimum pigment properties at a pH between 2 and 3. High concen-

trations of sulfuric acid were detrimental, and steps which increased the yield also tended to lower the quality of the product for pigment purposes.

Parravano and Caglioti [89] found that titanium sulfate solutions contained not only titanic and sulfate ions but also colloidal complexes of titanium dioxide and sulfuric acid. The proportions of the latter components depended upon the concentration and age of the solution and the temperature at which it had been maintained. By dialysis of such solutions, two types of gels were obtained. One was transformed by calcination at 850° C. into rutile, while the other, which was a powder, remained as anatase even after exposure to 950° C. for 1.5 hours. Concentration of titanium and titanium and sulfuric acid in the solution determined the two types of products.

The quantity of the metatitanic acid precipitated by thermal hydrolysis varied with the time of boiling and with the absolute and relative quantities of titanium dioxide and sulfuric acid in the solution. Its separation could be changed appreciably, however, by seeding with nucleating agents. Curves of the rate of change of the index of refraction of such solutions at various temperatures and concentrations showed a slight increase just before precipitation began. Pigmentary properties depended upon the temperature and concentration of the solution, the nature of electrolytes present, and the rate of formation of nuclei in the hydrolysis step. Precipitation conditions governed the nature and size of the micelle aggregates, and although the temperature and time of calcination controlled crystallization of the product and growth of the granules, the dimensions of the latter depended upon the size of the flocculates of the hydrolysis product. Conditions which led to precipitation of titanium dioxide of the anatase crystal form, having particles from 0.50 to 0.65 micron, were found to be the most effective for obtaining products of good pigmentary properties, while hydrolysis of solutions containing ferrous sulfate under conditions which led to the formation of rutile gave yellow products unsuited for white pigments.

Evaporation of hydrolyzing solutions of titanic sulfate showed reversibility of the reaction.[90] Resolution began as the acid value reached 12 to 17 per cent. Evaporation of such liquors changed two variables simultaneously—increased acidity of the medium, and raised the boiling point of the solution.

From a study of the equilibrium of the system titanium dioxide —sulfur trioxide-water at 100° C., Sagawa [91] concluded that the

thermal hydrolysis product of sulfate solutions was titanium dioxide with a small proportion of adsorbed sulfur trioxide and water, rather than a solid solution or a compound. A precipitate containing 2 to 5 per cent sulfuric acid and 3 to 5 per cent water was obtained by the hydrolysis of acid titanium sulfate, Ti (HSO$_4$)$_4$, and its sulfur trioxide content increased little with higher concentrations of acid in the liquor. Such solutions prepared by dissolving titanium hydroxide in sulfuric acid in some cases yielded titanium dioxide monohydrate on hydrolysis. The precipitation took place in the metastable state, however, since the concentration of titanic sulfate in the solution was far greater than in other systems which gave titanium dioxide.

The product precipitated by boiling sulfate solutions gave the X-radiograms of anatase.[92] Thermal dehydration isobars and X-ray analyses of different products indicated that the water was given off continuously and that no definite hydrates of titanium dioxide were formed.

Indirect Methods

Washburn and Aagaard [93] obtained practically pure titanium dioxide of pigment grade by an indirect process based on the method of producing coalesced composites by which thermal hydrolysis was effected in the presence of smaller proportions of extremely finely divided calcium sulfate which was later removed from the combined precipitate by washing with water. This was effective because of the much greater solubility of calcium sulfate than of titanium dioxide. The very large number of minute suspended particles having the anhydrite structure promoted and accelerated the hydrolytic decomposition of the titanium sulfate by breaking down the metastability of the solution by functioning as adsorptive nuclei for the compounds of titanium being precipitated. In this respect calcium sulfate acted somewhat after the nature of a catalyst; it also tended to prevent the occlusion of iron and to maintain an optimum particle size distribution.

As the reaction proceeds, sulfuric acid is one of the products of hydrolysis, and it is probable that, under the constantly changing conditions of concentration and total acidity of the solution, calcium sulfate may dissolve to some extent and precipitate to yield fresh, active particles. The anhydrite not only accelerated the hydrolytic precipitation of titanium to a much greater extent than the ordinary relatively insoluble extenders, but also yielded a pigment of excellent properties, e.g., color and opacity.

After reaction was complete, the precipitate was washed to remove the anhydrite. The solubility of calcium sulfate was much greater in salt solutions so that its removal from the hydrous titanium oxide was effected more rapidly by employing wash water containing an electrolyte, for example ammonium chloride.

To illustrate the method, a suspension of 25 pounds of hydrated lime in 32 gallons of water at 70° C. was added to 164 pounds of 78 per cent sulfuric acid. The anhydrite slurry thus formed was added to 1735 pounds of an ilmenite solution containing 6.07 per cent titanium dioxide, 5.88 per cent ferrous oxide, and 6.45 per cent free sulfuric acid, and the mixture was boiled until 95 per cent of the titanium was precipitated hydrolytically. The composite product was washed free of calcium sulfate, dried, and calcined at 900° C. to yield a pigment containing 99.1 per cent titanium dioxide and traces of calcium sulfate and other substances.

According to Washburn and Kingsbury,[94] the rate of hydrolysis of titanium sulfate was accelerated and a pigment of improved color and hiding power was obtained by heating the solution previously seeded with alkali-precipitated titanium hydroxide and carrying in suspension particles of calcium sulfate. Such nuclei were formed directly in the main body of the solution or in a separate portion by treating it with a base such as sodium carbonate, potassium hydroxide, calcium carbonate, ammonium hydroxide, or barium hydroxide. A proportion of the seeding compound amounting to 7 per cent of the total amount of titanium to be precipitated gave best results.

An extremely finely divided and effective calcium sulfate, having the structure of anhydrite, was obtained by adding a slurry of slaked lime or calcium carbonate to a slight excess of concentrated sulfuric acid and heating the resulting suspension near the boiling point to effect conversion of any hydrate formed.

In an example, an ilmenite solution containing 6 per cent titanium dioxide was prepared by dissolving the reaction product of the ore with concentrated sulfuric acid. All the iron was reduced to the ferrous condition, and the action was continued until a small proportion of the titanium was converted to the trivalent state. The suspended solids were coagulated and allowed to settle. Nuclear hydrous titanium oxide was precipitated by carefully pouring a solution of 6 kg. to 8 kg. of potassium carbonate into 26 liters of water at 80° C. upon the surface of 745 kg. of the clarified ilmenite liquor. The precipitate was immediately stirred into the solution, and the mixture was added to a slurry of anhydrite prepared by adding 11.3 kg. of hydrated lime suspended in 120 liters of water

to 93 kg. of 78 per cent sulfuric acid, both at atmospheric temperature. The charge was then boiled to effect hydrolysis of the titanium sulfate, and the mixed precipitate was washed free of calcium sulfate, and calcined to yield pure titanium dioxide of pigment grade.

Composite pigments may be prepared in the same manner by employing a higher proportion of calcium sulfate, or of a mixture of calcium sulfate and barium sulfate, and washing the product less so as not to remove the extender.

According to another process of this type,[95] a sulfate solution of ilmenite containing 50 g. to 250 g. titanium dioxide equivalent per liter was treated at atmospheric or slightly higher temperature with a hydroxide or carbonate of an alkali or alkaline earth metal or ammonium in a proportion just short of that required to react with all the potential sulfuric acid present. The term "potential acid" is applied to the free sulfuric acid, plus that combined with the titanium, and represents the total amount of acid that would be present in the solution after complete hydrolysis of the titanium sulfate. At this stage most of the iron remained in solution, while practically all the titanium was precipitated as orthotitanic acid. Employing an alkaline earth neutralizing agent, however, the corresponding insoluble sulfate was formed. The mixed precipitate was washed and digested with sulfuric acid to dissolve the titanic acid selectively, and the resulting suspension was filtered and washed to obtain a purified titanium sulfate solution. This was concentrated by evaporation under reduced pressure, and boiled at atmospheric pressure without nucleation to effect hydrolytic decomposition. The precipitate of hydrous titanium oxide was washed and calcined at 700° to 1000° C. to produce a pigment of high purity.

By carrying out the neutralization process in two steps employing an alkaline earth metal base which forms an insoluble sulfate, a purified solution of high concentration was obtained directly, thereby minimizing subsequent evaporation costs. This end was attained by adding calcium hydroxide or carbonate in the form of a slurry to the ilmenite solution in quantity short of that required to throw down the titanium. All the free sulfuric acid, and from 20 to 50 per cent of that combined as titanyl sulfate, was neutralized without precipitating the titanium. Free acid represents that part of the active acid over and above that required to form the titanyl salt with the titanium present. These relations may be expressed as

$$\text{Factor of acidity} = \frac{\text{Free acid} \times 100}{\text{Acid combined with titanium as titanyl sulfate}}$$

Such solutions were very basic and metastable. After filtration to remove the insoluble sulfates, the solution was treated with another portion of the alkali suspension, just sufficient to precipitate the titanium content. This method has the advantage of minimizing the amount of foreign matter included with the orthotitanic acid cake. Obviously, more concentrated purified solutions can be prepared from partially dehydrated cake, but this step must be carried out at low temperature to avoid decreasing the solubility of the titanium compounds.

In a specific test, to 5 liters of a solution containing 169.7 g. titanium dioxide, 44.2 g. iron, 522.0 g. total sulfuric acid, 236.4 g. free sulfuric acid and 444.4 g. active sulfuric acid per liter, and a factor of acidity of 114, was added a slurry of 1500 g. calcium carbonate in 10 liters of water at room temperature. The mixture was filtered and washed with 5 liters of 1 per cent sulfuric acid. The filtrate was then added to the wash liquor to get an intermediate solution containing 66.1 g. titanium dioxide, 17.3 g. iron as ferrous sulfate, 95.5 g. total acid, and 65.1 g. active acid per liter, and a factor of acidity of − 19.6. That is, the acid content was even less than that corresponding to the titanyl sulfate. The combined solution was heated to 60° C. and a slurry of 540 g. calcium carbonate in 3 liters of water was added, with stirring, to produce a precipitate which contained all the titanium, mixed with calcium sulfate. This product was filtered and washed and added to 900 ml. of concentrated sulfuric acid, with agitation. After cooling to room temperature, the calcium sulfate was filtered off and washed by repulping in 1 per cent sulfuric acid. The purified solution, consisting of the filtrate and washings containing 80.4 g. titanium dioxide, 13.7 g. iron, 208 g. total sulfuric acid, 85.5 g. free acid, and 184.0 g. active acid per liter, and having a factor of acidity of 86.8, was concentrated by evaporation under reduced pressure to corresponding values of 210.2 g., 42.5 g., 590 g., 258 g., and 515.5 g. per liter, which represented a factor of acidity of 99.7. On boiling for 4 hours at atmospheric pressure without seeding, this concentrated solution showed a yield of 91.5 per cent. The hydrous titanium oxide was filtered, washed, and calcined.

Analyses of the original, intermediate, and final solutions are shown in the table on page 195.

Booge [96] crystallized titanyl sulfate from solution at an elevated temperature and calcined the sulfate to produce the dioxide.

According to Lederer and Kassler,[97] a basic titanium salt free from contaminations of iron may be precipitated from a sulfate solu-

tion of ilmenite by introducing hydrogen sulfide, or a substance which will liberate this gas, together with a basic compound.

TABLE 7

ANALYSES OF SOLUTIONS

Property	Original Solution	Intermediate Solution	Purified Solution	Concentrated Solution
Total TiO_2 g. per liter.	169.7	66.1	80.4	210.2
Iron	44.2	17.3	13.7	42.5
Total H_2SO_4	522.0	95.5	208.0	590.0
Free H_2SO_4	236.4	− 15.9	85.5	258.0
Active H_2SO_4	444.4	65.1	184.0	515.5
Factor of acidity	114.0	− 19.6	86.8	99.7

A study of the hydrolysis conditions showed that commercially valuable titanium dioxide could be obtained from dilute solutions only if a considerable excess of sulfuric acid was present.[98] Zinc oxide increased the velocity of the hydrolytic reaction.

Ores Other Than Ilmenite

In a method of producing titanium dioxide pigment from natural rutile,[99] a finely ground mixture of the ore and magnesium oxide was first heated to form the titanate and this product was dissolved in aqueous sulfuric acid. The resulting solution was filtered and cooled to 0° C. to crystallize the magnesium sulfate, and the filtrate was heated to effect hydrolytic precipitation of metatitanic acid. This material was filtered, washed, and calcined according to accepted methods, and the sulfuric acid was recovered from the waste liquor.

Ryan and Knoff [100] fused finely ground rutile ore with an alkali metal compound, such as sodium hydrogen sulfate or potassium carbonate, in the proportion required to produce the corresponding acid-soluble titanate. This required the equivalent of 1 part sodium oxide to 5 parts of titanium dioxide. The reaction product was digested with 93 per cent sulfuric acid at 200° to 220° C. to convert the titanium component to soluble sulfates. These were dissolved in water, and the solution was clarified and run slowly into boiling water containing a small amount of oxalic acid to effect precipitation of hydrous titanium oxide.

A process employing siliceous ores of the sphene class was reported by Alessandroni,[101] who found that if the finely ground

material was heated with hydrochloric acid of more than 15 per cent strength, the titanium component was dissolved and held in solution along with the calcium and minor metallic constituents such as iron, magnesium, aluminum, and vanadium, leaving a residue primarily of silica. In operation the ore was heated with 10 to 20 per cent excess acid under a reflux at 40° to 50° C. for several hours to avoid loss of hydrogen chloride and inhibit hydrolysis until an appreciable amount of titanium had gone into solution. During the next 24 hours the temperature was raised gradually to the boiling point, and heating was continued until the optimum yield of titanium was obtained. The system was cooled, and the solution was separated from the siliceous residue by decantation and filtration and heated with sulfuric acid to convert the chlorides to sulfates. For reason of economy the hydrogen chloride liberated was recovered for future use. By controlling the temperature, concentrations, and method of mixing, anhydrite of pigment grade could be produced as one product. The suspension was filtered and the sulfate solution was concentrated by evaporation under reduced pressure to 10 to 20 per cent titanium dioxide and subjected to thermal hydrolysis by conventional methods to produce relatively pure titanium dioxide.

Composite pigments containing calcium sulfate or calcium sulfate and silica as extenders were obtained by leaving one or both of these components suspended in the titanium sulfate solution and carrying out the hydrolysis in their presence. As in other methods, any iron in the solution was reduced to the ferrous state.

By another approach, the clarified chloride solution from the extraction step was treated with sulfuric acid to convert the chlorides to sulfates, and the hydrochloric acid liberated was recovered and used to treat another batch of ore. The temperature, concentration, and method of mixing in this step were so controlled as to precipitate the calcium sulfate in the anhydrite form suitable for use as pigment. According to whether a pure titanium dioxide pigment or a composite product was desired, the calcium sulfate was removed or allowed to remain suspended in the solution. In either case the liquor was quite poor in titanium dioxide, in many cases below 5 per cent, and was concentrated by evaporation under reduced pressure to 10 to 20 per cent strength. Any free hydrochloric acid was removed at the same time, collected, and concentrated for reuse. The ratio of titanium dioxide to active sulfuric acid was adjusted to the proper value for the type of hydrolysis employed. All iron was reduced to the ferrous condition and a small proportion of the tita-

nium to the trivalent state. Thermal hydrolysis of the solution, and filtration, washing, calcination, and pulverization of the titanium dioxide were then carried out in the usual manner.

In an example, 1000 pounds of sphene analyzing 32.0 per cent titanium dioxide, 29.58 per cent silica, 18.65 per cent calcium oxide, 1.12 per cent magnesium oxide, 1.43 per cent ferrous oxide, 4.29 per cent ferric oxide, 12.94 per cent alumina, and 0.10 per cent manganese oxide was ground so that no more than 10 per cent was retained on a 100 mesh screen, then stirred into 8300 pounds of 29.5 per cent hydrochloric acid in a reaction vessel fitted with a reflux condenser. The mixture was then heated at 40° C. for 4 hours to avoid loss of free hydrochloric acid before the concentration had been appreciably reduced by reaction. During the next 24 hours the temperature was gradually raised to the boiling point, about 107° C. At this stage the reaction was practically complete, the system was allowed to cool, and the residue was removed by filtration. It weighed 372 pounds and consisted of 88 per cent silica, 6.5 per cent ferric oxide, and 5.5 per cent titanic oxide. The filtrate weighed 9100 pounds and analyzed 3 per cent titanium dioxide, 15.6 per cent free hydrochloric acid, and 4.06 per cent calcium chloride. This represented a recovery of 94 per cent.

One half the solution was mixed with 475 pounds of 93 per cent sulfuric acid to precipitate calcium sulfate, liberate free hydrochloric acid, and give a ratio of titanium dioxide to sulfur dioxide of 1.0 to 1.5. The calcium sulfate was removed by filtration, and the liquor was concentrated in a vacuum evaporator to 12 per cent titanium dioxide. At the same time the hydrochloric acid was completely driven off and recovered as a condensate. The concentrated solution was treated with zinc dust to reduce all iron to the ferrous condition and a small proportion of the titanium to the trivalent state, and subjected to thermal hydrolysis to precipitate the titanium as hydrous oxide which on washing, calcination, and pulverization by the usual methods gave a product of excellent pigment properties.

The other half of the solution was similarly mixed with 475 pounds of 93 per cent sulfuric acid to precipitate calcium sulfate, to liberate free hydrochloric acid gas, and to give a ratio of titanium dioxide to sulfur trioxide of 1.0 to 1.5. During this step the temperature was maintained above 70° C. to form calcium sulfate of the anhydrite crystal modification. The solution was then concentrated to 12 per cent titanium dioxide, and at the same time the remaining hydrochloric acid was driven off and recovered. It was then boiled

to effect thermal hydrolysis, and the mixed precipitate was washed and calcined to produce a high quality composite pigment containing 40 per cent titanium dioxide and 60 per cent calcium sulfate.

Perovskite [102] containing 40.8 per cent titanium dioxide, 30.7 per cent calcium oxide, and 5.2 per cent ferric oxide was converted to water soluble salts by heating the finely ground ore with twice its weight of 93 per cent sulfuric acid at 150° to 170° C. for 1 hour, and then at 150° C. for 1 hour more. Recovery of the titanium dioxide was 90 to 93 per cent. The mineral titanite [103] was likewise converted to a dry, water-soluble solid mass by digesting with 1.5 parts of 80 per cent sulfuric acid at 140° to 145° C. for 10 to 11 hours. The product was agitated with water at 97° C. for 7 hours, and metallic iron was added to the solution to reduce the ferric component to the ferrous state.

According to a process for producing titanium pigments from sphene [104] (titanite), the material ground to 200 mesh was mixed with 1.6 parts of hydrochloric acid as a 5 to 12 per cent solution and boiled under reflux to extract the soluble nonhydrolyzable constituents such as oxides of alkali metals and iron. Employing acid of this concentration, any titanium that dissolved was immediately hydrolyzed at this temperature and precipitated as hydrous oxide. Such a treatment required 72 hours for completion and yielded a solution containing calcium, magnesium, iron and manganese and other constituents which form nonhydrolyzable salts, and a residue consisting essentially of the titanium dioxide, silica, and alumina of the original ore. The undissolved portion was then removed from the liquor by decantation or filtration, washed, and dried. A partial mechanical separation was effected at this stage by selective dispersion in water with such agents as chlorides of aluminum, titanium, cerium, and zirconium which dispersed the titanium oxide to a greater degree and held it in aqueous suspension for a longer period of time than the impurities. The titanium-containing residue was agitated for 1 or 2 hours with water containing 0.5 to 5 per cent aluminum chloride (based on the solids) to form a uniform free-flowing slurry. Stirring was then discontinued and the mixture was allowed to stand until the silica and other impurities settled; this took place fairly rapidly. The suspension of hydrous titanium oxide was separated by decantation or elutriation, coagulated with magnesium sulfate, and filtered. In either operation the concentrate was dissolved in strong sulfuric acid to form solutions from which pure oxide was precipitated by thermal hydrolysis.

In an example, 150 pounds of finely ground sphene containing 32 per cent titanium dioxide was added to 180 gallons of 12 per cent hydrochloric acid at room temperature and boiled under reflux for 48 hours. The residue was separated from the supernatant liquor by filtration, washed, and dried. Analysis showed 46.2 per cent silica, 5.7 per cent ferric oxide, and 48 per cent titania which represented 98.8 per cent of the titanium in the original ore. One half the residue was heated with an equivalent amount of concentrated sulfuric acid, and the reaction product was leached with water to obtain a solution of titanium sulfate. All the insoluble material, largely silica, was separated, and the solution was treated with zinc dust to reduce the iron salts to the ferrous condition and a small proportion of the titanium to the trivalent state. It was then subjected to thermal hydrolysis and the precipitate of hydrous titanic oxide was washed, filtered, calcined, and pulverized. The other half of the original residue was treated in the same manner, except that the silica was not separated from the solution before hydrolysis. This gave a composite pigment consisting of approximately equal parts of titanium dioxide and silica.

Anderson and Williams [105] sintered an intimate mixture of titanium silicate mineral (sphene) with limestone and sodium sulfate, leached the cooled product with water, and treated the clarified solution with carbon dioxide to precipitate titanium hydroxide.

According to a method developed for processing Japanese iron sands containing titanium and vanadium, the solution obtained by dissolving the finely divided material in sulfuric acid was first diluted with water to 10 times the volume of the original ore and treated with scrap iron to neutralize the excess acid.[106] By thermal hydrolysis 93 per cent of the titanium was precipitated from the clarified solution as hydrous oxide. Iron was recovered from the filtrate by crystallization as ferrous sulfate, and the vanadium was obtained from the evaporated liquor as the pentoxide.

Indian bauxites normally contain from 9 to 12 per cent titanium dioxide. A method for the recovery of this constituent from residual muds after the manufacture of aluminum sulfate was described by Chakravarty.[107] Such muds were first heated with dilute sulfuric acid to dissolve most of the remaining iron, then washed with water, dried, and pulverized. After this purification step, the residue was digested with strong sulfuric acid and the reaction product was dissolved in water. The solution was clarified, treated with scrap iron to reduce the ferric sulfate to the ferrous salt, and boiled to effect

hydrolytic precipitation of the titanium sulfate as hydrous oxide. This product was filtered, washed, and calcined. From 100 pounds of mud was obtained 42 pounds of 98 to 99 per cent titanium dioxide suitable for white pigment, vitreous enamel, and soap making.

Swarup and Sharma [108] obtained a 75 per cent recovery of titanium dioxide of 99 per cent purity from the red mud left behind in extracting aluminum oxide from Indian bauxites. The mud was calcined and mixed with sulfuric acid of specific gravity 1.6. Steam was passed in until the specific gravity was reduced to 1.1, and then the product was filtered and washed. This titanium-rich residue was treated with sulfuric acid of specific gravity 1.6, and steam was passed in until the temperature reached 60° C. The liquor was diluted with water to a specific gravity of 1.2 and filtered. Scrap iron was introduced to reduce all ferric ions to ferrous, and the solution was hydrolyzed after adding freshly prepared titanic hydroxide nucleating agent.

According to another modification, the air-dried sludge was treated with sulfuric acid of specific gravity 1.4 at 80° to 90° C., and the titanium-rich residue was separated, washed, dried, mixed with sulfuric acid of specific gravity 1.89, and heated at 250° to 300° C. in a muffle furnace. [109] The reaction product was dissolved in water, and the solution was clarified and hydrolyzed according to conventional methods. Densai and Peermahomed [110] digested bauxite sludge with 10 normal sodium hydroxide at 100° C., then heated the washed and dried product with concentrated sulfuric acid for 8 hours at 130° C. Iron filings were added to reduce the iron component and part of the titanium to the next lower state of oxidation, and the solution was filtered and heated at 100° C. to effect hydrolytic precipitation of H_2TiO_3. The precipitate was filtered, washed with dilute sulfuric acid, water, dilute sodium hydroxide solution, and again with water, then calcined to produce a snow-white product containing 97 per cent titanium dioxide.

Chapter 12

FILTERING AND WASHING HYDROUS TITANIUM DIOXIDE: ACID RECOVERY

Filtering, Washing, and Bleaching Hydrous Titanium Dioxide

'Regardless of the type of pigment produced, the filtration and washing procedures are very similar. At the end of the hydrolysis step the system consists of hydrous titanium dioxide suspended in a strongly acid sulfuric acid liquor which also contains a large proportion of ferrous sulfate and small amounts of other dissolved salts. Added extenders may also be suspended in the liquor. Separation of the precipitate from the liquor may be effected by repeated decantation, but this would result in a dilution of the liquor to such an extent that acid recovery would probably be uneconomical and at best would be slow and cumbersome.

On the other hand, direct filtration requires special acid-resistant filters and filter media, but in commercial operation this method is usually employed. Filters of various types coated with paper pulp and diatomaceous earth, nitrated cloth, perforated rubber, glass cloth, vinylite cloth, or similar materials have been employed.

Hydrous titanium oxide for pigment manufacture is precipitated normally by the thermal hydrolysis of sulfate solutions of ilmenite in which the iron content is maintained in the ferrous state. Although under these conditions there is no hydrolytic decomposition of the ferrous compounds, the freshly precipitated titanic oxide always carries entrained with it a small amount of iron in the ferrous condition, together with adsorbed or combined sulfuric acid.

Prolonged washing, consisting of a number of filtration, reslurrying, and refiltering operations, is effective in removing all the iron and other foreign salts except those adsorbed by the pulp. The adsorbed iron salts cannot be completely removed by washing with water alone, apparently because they are oxidized to the trivalent state during the operation, and ferric compounds are adsorbed to a much greater degree than ferrous compounds. At any rate it is not possible by this means to reduce the iron content of the pulp much

below 0.1 per cent, or the adsorbed or combined sulfuric acid below 5 to 8 per cent. Although this proportion of iron does not render the products unsuited for industrial use, greater purity is desired to obtain pigments of improved whiteness.

If this washing operation is followed by treatment with a 0.5 to 5 per cent solution of sulfuric or hydrochloric acid at higher temperatures (50° to 60° C.), pulps practically free from iron can be obtained. In an actual test, 1 gram hydrous titanium oxide, after washing five times with cold water, retained 50 mg. ferric oxide; another sample washed four times with cold water and once with cold 1 per cent sulfuric acid contained 20 mg. ferric oxide; while a third sample washed four times with cold water and once with 1 per cent sulfuric acid at 50° C. retained only 0.5 mg. ferric oxide.

To illustrate, the hydrous titanic oxide precipitated from a sulfuric acid solution of ilmenite was filtered from the mother liquor and washed with cold water until only a very small amount of iron compounds remained. It was then made into a paste of 1 part titanium dioxide to 1½ parts of 1 per cent sulfuric acid. The mixture was heated at 50° C. for 1 hour, filtered, and again washed rapidly with cold water.[1] Good results were obtained by carrying out the washing operation on filters of calcium sulfate or barium sulfate.[2] The hydrous oxide was washed alternately with cold water and hot dilute acid.

The iron content was reduced to still lower proportions (0.0005 to 0.001 per cent ferric oxide) by subjecting the pulp to a digestion treatment in the presence of added sulfuric acid and a reducing agent, such as a titanous salt, sulfur dioxide, or a soluble thiosulfate or sulfide.[3] The titanous compound may be formed in place by adding metallic zinc to the acid-pigment slurry. Precipitated hydrous titanic oxide was washed with water and suspended in a solution of 4 to 12 per cent sulfuric acid, the reducing agent was added or formed in place, and the mixture was heated at 60° to 90° C., with agitation, for 6 to 8 hours and in some instances up to 24 hours. After this treatment the pulp was filtered and washed with water to remove the remaining iron salts.

Washed, hydrolytically precipitated titanium dioxide was digested in an 80 to 120 g.p.l. sulfuric acid solution at a temperature of 80° C. to the boiling point for several hours to remove absorbed and adsorbed impurities.[4] This process was particularly effective in removing compounds of vanadium, chromium, and iron, which, if present in extremely small proportions, discolor the pigment. A small

amount of titanium was also dissolved. The purified titanium oxide was separated from the acid liquor, washed with water, and calcined.

De Rohden [5] digested hydrolytically precipitated titanium dioxide with dilute hydrochloric acid in the presence of a reducing agent (hydrogen sulfide or soluble thiosulfate) to remove the iron and obtained a pigment of improved color. This bleaching effect was also obtained by digesting the hydrous oxide in an aqueous 1 per cent solution of hydrochloric acid containing a small proportion of an alkali metal salt of an oxygen acid of chlorine, such as sodium hypochlorite or potassium chlorate. [6]

Iron compounds and similar impurities may be washed from crude titanic acid after reduction with sulfur dioxide or sulfites. [7] The proportion of the agent employed should correspond not only to the trivalent iron but also to the oxidants present. Sulfur dioxide does not reduce tetravalent titanium (to the trivalent state) so there is no loss of this element in the acid liquor as titanous salts are not precipitated in the hydrolysis step. Care should be taken to prevent reoxidation of the ferrous compounds during subsequent washing. Titanic acid produced by decomposing ilmenite with alkalies was freed from iron by heating for several hours with dilute mineral acid (10 to 30 per cent sulfuric acid) in the presence of reducing agents such as titanous sulfate or sulfurous acid. [8] The acid was of such a strength as not to dissolve the titanium component.

Although the last trace of iron may be removed by digesting the washed pulp with dilute sulfuric acid in the presence of a reducing agent at an elevated temperature with agitation for 6 to 24 hours, this treatment requires a break in the washing process and acid must be added to the system. However, by mixing powdered zinc with the hydrous titanic oxide during the first repulping operation after separation from the strongly acid hydrolysis liquor, reducing conditions may be maintained throughout the washing process without the necessity of a special reduction step. [9] Residual acid is sufficient to effect the reaction. By this treatment a small proportion of titanous salts is formed which prevents oxidation of the ferrous compounds and thus permits their complete removal by the regular washing process. This operation also facilitates removal of other reducible impurities such as traces of chromium and vanadium originally present in the ore.

As an illustration, the hydrolysis product, consisting of a suspension of hydrous titanium oxide in a solution of sulfuric acid and ferrous sulfate, was filtered on a rotary vacuum or leaf filter which

consisted of a series of frames, each carrying an acid-resisting covering. The cake was removed and agitated with the least amount of water to give a free-flowing slurry, and sufficient powdered zinc was added to maintain reducing conditions throughout the remainder of the washing operation and prevent oxidation of any of the iron to the ferric state. Enough closely held acid was retained by the pulp to react with the zinc. The slurry was then filtered on a rotary or leaf filter. The cake was reslurried with additional fresh water and refiltered and repulped a number of times until the impurities were removed. One addition of zinc maintained reducing conditions throughout the entire step and permitted removal of iron without interrupting the washing operation. Furthermore, no variation in the regular practice was required and no acid was added to the system. Pigments obtained from pulps treated in this manner had a high degree of whiteness and brightness. Other properties were also greatly improved.

To improve the color of the finished pulp, hydrous titanium oxide prepared from ilmenite solutions has been treated during the washing operation with a solution of a salt of thorium, zirconium, or aluminum to displace the iron present as impurity.[10] On calcination, these compounds produced white oxides in contrast to the reddish brown of ferric oxide.

The color of the pigment may be improved by subjecting the washed hydrolysis product to a bleaching treatment to reduce the compounds of vanadium, chromium, manganese, and other impurities to a minimum.[11] These hang with the pulp through ordinary washing with water. Nine parts of a slurry of 300 g. hydrolytically precipitated and washed titanium dioxide per liter was mixed with 1 part by volume of 60° Bé sulfuric acid and the resulting mixture, containing 270 g. per liter titanium and 135 g. per liter sulfuric acid, was heated to 90° C. and held for 1 hour. It was then cooled, filtered, washed, and calcined as usual. This pigment was noticeably better in color than a similar product in which the sulfuric acid treatment was omitted. Only 0.5 per cent of the titanium dioxide was dissolved. Chromium compounds[12] most affect the color, and the limit of sensitivity to the eye is 1.5×10^{-6} parts of the oxide in 1 part of titanium dioxide. To overcome such discoloration, the pigment was mixed with an alkali metal carbonate, oxide, or hydroxide, or with an alkaline earth metal oxide, in a proportion slightly in excess of that required to react with all the chromium present, roasted at an incandescent heat, and washed to remove the chromate formed. If magnesium or barium oxide is used, an insolu-

ble chromate is formed which is very slightly colored and may be left in the pigment without serious injury. The alkali chromates are soluble in water, while those of the alkaline earth metals are insoluble in water but soluble in dilute acids so that the leaching procedure depends upon the type of chromate formed. Oxidizing agents may be added before the roasting step.[13]

A process for washing hydrolysis product containing iron and copper salts was reported by Allan.[14] The hydrous titanium dioxide, after separation from the mother liquor, was washed first under reducing conditions until practically all the iron was removed. It was then treated with an oxidizing agent such as nitric acid or hydrogen peroxide to convert the copper to the soluble cupric state, in which form it was readily removed by further washing with water.

In a commercial process described by Brown[15] the hydrous titanium oxide was first separated from the hydrolysis liquor containing high proportions of sulfuric acid and ferrous sulfate by filtration on a Sweetland press, then washed to remove most of the foreign materials. It was then reslurried in water and further washed on a series of Oliver continuous filters. At the Chelyabinsk pigment plant, in the Union of Soviet Socialist Republics, microporous rubber[16] has been employed as a filtering medium. Mean diameter of pores was of the order of 10^{-4} mm., although the openings can be made as small as 10^{-7} mm., according to the method of manufacture. Glass cloth, nitrated cloth, and synthetic resin cloth have also been recommended as media for the first filtration, but, after initial separation from the strong hydrolysis liquor, further filtrations and washings may be carried out on cotton fabric media.

Neutralization of Residual Sulfuric Acid

Hydrous titanium dioxide precipitated by the thermal hydrolysis of sulfate solutions retains around 5 to 10 per cent sulfuric acid even after thorough washing with water, and it may be desirable to remove or neutralize this closely held acid before calcination. Many methods have been proposed for accomplishing this end, but, in general, alkali metal or ammonium hydroxides are added to form neutral salts which may be washed out readily. The ammonium salts may be removed by volatilization at elevated temperatures. Alkaline earth metal compounds, oxides, hydroxides, or chlorides may be added to form insoluble sulfates which are retained in the precipitate. The latter method is particularly applicable to composite-pigment pulps. For example, by adding lime slurry to titanium dioxide-anhydrite

pulp the residual acid will be recovered in the final pigment as calcium sulfate.

Neutralization or removal of this closely held acid is not necessary, however, for at the temperatures normally employed in calcination, 950° to 1050° C., it would be driven off along with the water content. If desirable, this sulfur trioxide can be recovered from the stack gases by electrolytic Cottrell precipitators.

Jebsen [17] neutralized the residual sulfuric acid by agitating the pulp with an excess of a hydroxide or carbonate of an alkali metal or ammonium, and removed the resulting neutral salts by washing with water. Similarly, by treating the hydrous oxide slurry with aluminum hydroxide, zinc hydroxide, sodium aluminate, or sodium zincate, the acid was converted to soluble salts which were readily washed out.[18] Monk and Ross [19] treated the washed hydrolysis product with ammonia or other volatile base, such as aliphatic amines, and then heated the mixture to a comparatively low temperature to remove the products of reaction (ammonium sulfate) by volatilization, and finally up to 1000° C. to effect crystallization of the titanium dioxide. Alternatively, the hydrous oxide was dried at 100° to 700° C. without decomposition before introducing the basic material. To conserve the alkaline neutralizing agent, the hydrous titanium oxide was first dried and then subjected to the action of a basic gas (ammonia) and heated in air to 500° to 1000° C. to remove the sulfate compounds.[20] In a two-stage process the pulp was first treated with an alkali to combine with only a part of the residual acid, and the remainder was neutralized by kneading the mass with 5 per cent zinc oxide.[21] The product was washed, dried, and heated to incandescence to develop pigment properties.

The combined or adsorbed sulfuric acid may be transformed into neutral insoluble salts by treating the washed hydrolysis product with hydroxides, carbonates, or soluble salts of alkaline earth metals, such as calcium hydroxide and barium chloride.[22] Employing chlorides, the hydrochloric acid should be washed out before calcination. This treatment may be conveniently effected by adding a slurry of the alkaline earth base to the pigment pulp, also as a slurry, with thorough agitation, after which the product should be dewatered on a suitable filter.

Acid Recovery

A practical method for the recovery of sulfuric acid from dilute waste liquors obtained in the manufacture of titanium dioxide pigments was developed by McBerty.[23] In the most common process

for the production of such pigments, ilmenite ore is attacked with strong sulfuric acid and the reaction product is dissolved in water. All of the ferric component is reduced to the ferrous state, and a large proportion is crystallized out as copperas on cooling the solution. The resulting sulfate liquor, containing small amounts of iron and other impurities such as chromium and vanadium, is finally hydrolyzed to precipitate the titanium as hydrous oxide. At the same time an equivalent amount of sulfuric acid is liberated, and the filtrate contains from 10 to 30 per cent sulfuric acid, appreciable amounts of ferrous sulfate, some titanium, and most of the soluble impurities originally present in the ore.

In the first step of the recovery process, this dilute waste acid liquor was concentrated to such a degree that it became saturated with ferrous sulfate at a temperature near its boiling point but short of precipitation. This operation was conveniently carried out in a vertical tower with a countercurrent of hot gases from the next step. Spent gases and water vapor from this operation were wasted into the atmosphere. Up to the end of this stage the liquor remained free flowing and contained 30 to 40 per cent sulfuric acid and 12 to 20 per cent ferrous sulfate. It was further heated until the dissolved copperas was converted to the monohydrate, but not to the point at which sulfuric acid distilled off. Ferrous sulfate, crystallized originally from the ilmenite solution, was added at this stage and likewise converted to the monohydrate. Heat required for this operation was derived from the combustion of carbonaceous fuel and the hot gases traveled countercurrent with the liquid. The most convenient form of apparatus was found to be a brick-lined rotary kiln, although the concentration may be carried out in a vacuum evaporator of the Mantius type. A considerable proportion of monohydrate crystallized out, leaving a liquor containing 65 to 80 per cent acid. If there was a demand for cheap technical-grade sulfuric acid of this concentration, the product of this stage was cooled to crystallize most of the iron compounds and other impurities. At an acid strength of 65 per cent, the precipitate of monohydrated ferrous sulfate entrained with it about 50 per cent of the chromium and 75 per cent of the vanadium present. However, if the concentration was carried to 80 per cent, it became almost impossible to separate the acid from the ferrous sulfate by physical means (filtration), and the resulting sludge was heated in a brick-lined rotary furnace below 300° C. to distill off all free sulfuric acid. This temperature range was maintained as long as appreciable amounts of acid remained, and the ferrous sulfate was incompletely oxidized, since at 300° C.,

or above, strong sulfuric acid reacted with ferrous sulfate to form the ferric salt and sulfur dioxide. The acid vapors were condensed in the conventional apparatus, yielding a product of 65 to 85 per cent strength. Little decomposition took place. Distillation was carried out in an oxidizing atmosphere to further aid conversion of ferrous iron to the trivalent state and thereby minimize losses due to decomposition of iron sulfates at the relatively low temperatures. Heat for this step was provided by hot gases produced by the combustion of carbonaceous fuel, elemental sulfur, or sulfide ores in an excess of air. The hot gases were led into contact with the iron sulfate sludge, and after condensation of the sulfuric acid the exit sulfur gases were conducted to a sulfuric acid plant. The solid residue from this stage, a more or less basic ferric sulfate, was heated in another rotary kiln above 700° C. by direct contact with hot gases derived from the combustion of sulfur or pyrite. A strongly oxidizing atmosphere was maintained to increase the yield of sulfur trioxide, since oxygen in the presence of ferric oxide tends to shift the equilibrium of the reaction, $2SO_2 + O_2 \rightleftarrows 2SO_3$, to the right. Gases from this step contained a considerable proportion of sulfur trioxide and variable amounts of sulfur dioxide, depending upon whether sulfur or carbonaceous fuel was used. Such gases were freed from sulfur trioxide and suspended particles of iron oxide before conversion in a contact-acid plant, otherwise the impurities would greatly reduce the effective life of the catalyst. For this reason the gases were converted to sulfuric acid in a lead-chamber plant.

The residue consisted primarily of a reddish-brown ferric oxide suitable for use as pigment or as an ore of iron. It also contained the vanadium and chromium values of the original ore, and these constituents were recovered by chemical means.

In a typical operation, a waste liquor containing 25 per cent sulfuric acid and 11 per cent ferrous sulfate was concentrated in a vertical tower, with hot countercurrent gases from the next advanced step, to 32 and 14 per cent respectively, and the discharge from this operation was further concentrated to 65 per cent sulfuric acid by heating at 153° C. At this stage the greater part of the ferrous sulfate separated as the monohydrate and was filtered off. The filtrate of 65 per cent acid, which contained only small amounts of dissolved iron and other metallic impurities, represented 65 per cent of the total free acid. The filter cake containing the other 35 per cent was charged into a direct-fired rotary kiln and free sulfuric acid was distilled off and condensed. Hot gases from the combustion of low-grade fuel oil were passed in direct contact with the sludge so

that its temperature did not exceed 300° C. An oxidizing flame was maintained to prevent reduction of sulfuric anhydride to sulfur dioxide. In this operation, 95 per cent of the free acid was distilled off and recovered at a 65 per cent strength. The oxidized iron sulfate from the previous step was further heated in a direct-fired rotary kiln at 700° C. in an oxidizing atmosphere, and the discharge gases, containing 6.5 per cent sulfur trioxide and 2.25 per cent sulfur dioxide, were converted in a chamber sulfuric acid plant.

Spangler [24] described a commercial method comprising the contact process for recovering the sulfuric acid values from spent liquors from titanium pigment manufacture. Such solutions normally contain 18 to 25 per cent sulfuric acid, 10 to 16 per cent ferrous sulfate, and small amounts of titanium sulfate. The free acid was first neutralized with iron oxide, which was obtained from a subsequent step of the process, and the resulting solution was evaporated to recover anhydrous iron sulfate. Both neutralization and evaporation were safely carried out in one rotary kiln heated internally by combustion of gases. The iron sulfate residue was then decomposed in a rotary roaster to produce sulfur dioxide gas of the proper concentration for subsequent conversion in a contact acid plant, and ferric oxide cinder, a part of which was returned for the neutralization of additional batches of waste liquor. After purification, the sulfur dioxide was converted to sulfuric acid of any desired strength in a modified form of the standard Chemico contact acid plant using vanadium catalyst. This procedure, using dehydrated iron sulfate, was similar to the conventional contact process employing pyrite or sulfur, except that a heating and reducing agent was added to the raw material. Low-grade fuel oil or pulverized coal proved quite satisfactory, and pyrite was mixed with the sulfate residue, thus supplying part of the heat required and at the same time producing sulfur dioxide to enrich the roaster gases. A plant of this type was constructed for the National Lead Company, Titanium Division, in 1936.

Residual waste solutions containing 124 g. per liter sulfuric acid and 110 g. per liter ferrous sulfate were treated with ferrous sulfide, and the hydrogen sulfide evolved was oxidized first to sulfur and then to sulfur dioxide and used to produce sulfuric acid. [25] The liquor was added to a solution of calcium hydrosulfite to precipitate calcium sulfate and ferrous sulfide, which were separated, mixed with petroleum coke, and roasted at 300° C. to convert the calcium sulfate to sulfide. The ferrous sulfide remained unchanged. These mixed sulfides slurried in water were transferred to an autoclave, hydrogen sulfide was introduced at a pressure of 5 p.s.i., and the resulting

calcium hydrosulfide solution was separated by filtration. Part of the ferrous sulfide was used to treat more waste acid liquor. The remainder was roasted to produce sulfur dioxide for the manufacture of sulfuric acid. The calcium hydrosulfide was used to treat more ferrous sulfate solution, thus completing the cycle.

In a continuous process, crystalline ferrous sulfate was heated with air to effect decomposition, and the gaseous mixture was passed into a lower temperature zone to favor oxidation of sulfur dioxide to the trioxide.[26] Additional cold air was introduced to take up the heat liberated in the oxidation reaction and hold the temperature within the effective range. In a two-step dehydration process, crystalline ferrous sulfate was first heated at 80° to 167° C., under non-oxidizing conditions, to form the monohydrate and then at 167° to 492° C., in contact with air, until the anhydrous basic sulfate was formed.[27] The anhydrous salt was heated at 700° C. to yield sulfur dioxide and sulfur trioxide, free from moisture and iron oxides. The last trace of basic ferric sulfate was removed from the iron oxide by heating with charcoal.

Heinrich [28] concluded that the recovery of dilute waste sulfuric acid from the manufacture of titanium pigments could hardly be justified from a standpoint of economy, but avoidance of damage and stream pollution must also be considered. In certain localities the law would not permit the dumping of large amounts of sulfuric acid.

Titanium dioxide is more sensitive to discoloration by chromium compounds than by any other ordinarily encountered impurity,[29] and since recycled sulfuric acid tends to pick up this constituent from the ore, it should be removed before each reuse of the acid. This may be accomplished readily after concentration to 92 per cent sulfuric acid.[30] Crude acid of this strength was heated to 300° C. to convert the chromium to an insoluble compound, in which form it was readily recovered by settling or by filtration. According to a similar procedure, the waste liquor was concentrated by evaporation to 60 per cent sulfuric acid to precipitate most of the ferrous sulfate, and oleum or sulfur trioxide was added to raise the acid content to 88 per cent.[31] At this concentration the metallic impurities precipitated.

Spent liquor containing more than 20 per cent sulfuric acid, together with small amounts of titanium, zirconium, and hafnium compounds, was purified by treatment with phosphates as superphosphate.[32] The resulting precipitate was separated by any convenient means. Such solutions were preliminarily decolorized [33] by treatment with active carbon or sulfur dioxide, or by precipitation,

after which the oxide or carbonate of barium was added to obtain a precipitate of barium sulfate free from iron. The reaction was facilitated by adding a small proportion of nitric, hydrochloric, or acetic acid, or of one of their salts, to produce a soluble barium compound.

Waste acid liquor was purified sufficiently for use in the production of pigment-grade calcium sulfate or titanium dioxide by treating it with a soluble alkali metal chloride, sulfate, phosphate, or chlorate ranging in amount in gram atoms of alkali metal per liter of solution treated from 2 to 5 times the reciprocal of the percentage by weight of sulfuric acid.[34] The resulting precipitate was removed by settling or by filtration. Calcium sulfate and titanium dioxide pigment obtained with the use of the concentrated but unpurified waste acid differed very materially from that produced in processes employing relatively pure commercial acid. For one thing, such products were characterized by an objectionable yellowish or yellowish-brown tone which rendered them wholly unfit for many industrial uses. Furthermore, sulfuric acid costs constitute a major item of expense in titanium pigment manufacture, and it is obvious that losses occurring by reason of waste acid discard would be a serious economic factor in the process. Besides, disposal of the waste acid would constitute a serious nuisance problem.

In a typical test, 10 g. of sodium sulfate was added to 1 liter of waste hydrolysis liquor which weighed 1280 g. and contained 296.2 g. free sulfuric acid, 16 g. titanyl sulfate, and 66.7 g. ferrous sulfate. Expressed as gram atoms of sodium per liter of acid solution, this was 3.26 times the reciprocal of 23.14, the percentage of sulfuric acid in the waste liquor. The mixture was agitated for 1 hour at room temperature, and the resulting precipitate, 12 g., was filtered off. Calcium sulfate prepared from the filtrate was practically equivalent in every respect to a similar product prepared from fresh acid.

Another portion of the purified acid was concentrated to 82 per cent strength, mixed with a suitable amount of fresh 98 per cent acid, and employed in attacking ilmenite by the conventional method. The resulting pigment was equivalent to that obtained under the same conditions but employing relatively pure fresh acid.

Parrish[35] neutralized the waste acid solution with gas-plant liquor, ammonium hydroxide, to form ammonium sulfate and oxides of iron. Hydrogen sulfide and carbon dioxide gases were liberated in the process. Similarly, gaseous ammonia was added to ferrous sulfate solution to precipitate ammonium sulfate and a basic iron compound.[36] The precipitate was separated and heated to 140° C.

to convert the iron compounds to insoluble form, and the ammonium sulfate was dissolved in water. Platonov, Zakharova, and Efros [37] recovered vanadium from the waste liquors by precipitation with ammonium hydroxide.

The residual sulfuric acid of the washed titanium dioxide pulp, as obtained commercially by hydrolysis of sulfate solutions, is driven off in the calcination step as sulfur trioxide and may be recovered from the stack gases by precipitators of the Cottrell type.

Chapter 13

COMPOSITE PIGMENTS

The earliest titanium pigments were composites prepared by adding alkaline agents to sulfuric acid solutions of ilmenite so as to precipitate the hydrous oxide on the suspended extender particles added as such or formed in place by reaction with the sulfate component of the liquor. Some improvement was made by adding smaller proportions of alkaline earth bases to form the corresponding insoluble sulfate, but short of the amount required to react with the titanium, and the latter was later precipitated by thermal hydrolysis. By another method, alkaline earth chlorides were added to form the insoluble sulfate extenders, and the mixture was heated to precipitate hydrolytically the resulting titanium chloride.

Properties of these composites were short of expectations, and further developments revealed that much better products could be obtained by thermal hydrolysis of ilmenite solutions in the presence of suspended alkaline earth sulfates prepared separately so as to develop certain and specific properties. In preparing calcium sulfate of this grade, a slurry of hydrated lime was added to sulfuric acid under carefully controlled conditions of concentration and temperature so as to get a finely divided product of the anhydrite crystal form. Barium sulfate was prepared from the mineral barite. The pulverized ore was roasted with powdered coal to form soluble barium sulfide, which was leached from the reaction product. Aqueous sodium sulfate was then added to the clarified solution to precipitate the barium sulfate in a finely divided form and the product was filtered and washed. Depending upon the type of pigment to be made, the extender in the form of a heavy slurry was suspended in ilmenite solution in such proportions that the final product contained approximately 30 per cent titanium dioxide, and the solution was boiled to precipitate the titanium as hydrous oxide on the suspended particles. The ratio of the original constituents was determined more or less empirically.

Later methods were developed whereby such pigments, having equal properties, could be produced by blending in the wet or dry state precalcined titanium dioxide of pigment grade with barium

sulfate, calcium sulfate, or other extender especially prepared for this purpose. The thoroughly mixed composite was dried and recalcined, after which it was finished in the conventional manner.

Coalesced Composites

Barton [1] found that by precipitating orthotitanic acid from sulfate solutions containing extenders such as barytes, silica, china clay, asbestine, and calcium sulfate, the gelatinous material fixed itself to or coalesced with the suspended particles. The washed composite product on calcination was soft and fine grained and had good pigment properties, in contrast to the hard and gritty material obtained in a similar manner from orthotitanic acid without the extenders. In one modification the extender was suspended in the solution and an alkaline compound, such as sodium hydroxide, potassium carbonate, or sodium sulfide, which yield soluble sulfates, was added to precipitate the orthotitanic acid on the added particles. Better results were obtained by treating the solution with a reagent capable of acting both as a precipitant of orthotitanic acid and of supplying the extender by reaction with the sulfuric acid present. Calcium hydroxide, barium hydroxide, and barium sulfide are examples of this group of compounds. Before precipitation, copper and other heavy metal compounds present as impurities, which yield sulfides insoluble in dilute acid, were removed from the solution by passing in hydrogen sulfide. Iron, if present, precipitated along with the pigment materials but redissolved on treating the suspension with sulfur dioxide.

In an example, a solution containing 10.7 per cent titanium dioxide, 0.85 per cent ferric oxide, 1.78 per cent sodium oxide, and 25.3 per cent sulfur trioxide was prepared by dissolving crude hydrous titanic oxide in sulfuric acid. The iron component was reduced electrolytically to the ferrous state, and the sulfuric acid content was adjusted so as to give a pigment of the desired composition. A slurry prepared by slaking 11.6 parts of calcium oxide in 6 parts of water was added, with stirring, to 140 parts of the original solution, and the mixture was heated at 85° to 95° C., with agitation, for 1 hour. The composite precipitate was washed, dried, and calcined at 750° C. to give a pigment composed of 27 per cent titanium dioxide and 73 per cent calcium sulfate, with a trace of iron. Iron could be precipitated from the impure solutions before treatment with the alkaline earth compound by adding sodium sulfide or a mixture of hydrogen sulfide and sodium hydroxide.[2]

In an improved process, the alkaline earth base was added to the titanium sulfate solution to form insoluble sulfates, but short of the amount required to react with all the titanium and iron present. The mixture was then heated to precipitate the titanium as hydrous oxide on the suspended sulfate particles.[3] If the original solution did not contain enough sulfate radical to yield the desired proportion of insoluble sulfate in the finished pigment, additional sulfuric acid was introduced before treatment with the calcium or barium hydroxide.[4] The solution was boiled to precipitate the titanium hydrolytically on the suspended particles. Rossi[5] treated the original solution with an extract of leaves or bark or other organic material, and added calcium hyroxide to neutralize the excess sulfuric acid present. The charge was then boiled to effect hydrolysis of the titanium compounds, and the precipitate was washed and calcined to produce a composite pigment. Addition of organic matter to the crude solution not only accentuated and accelerated precipitation of the titanic oxide, but also minimized the precipitation of impurities.

Preliminary experiments by Soviet workers[6] showed that in the hydrolysis of titanium sulfate with calcium carbonate, a highly dispersed mixture of titanium dioxide and calcium sulfate was formed. In X-ray patterns and physical properties the precipitated pigments were different from those obtained from mechanical mixtures and were superior in covering power.

By another approach a chloride of calcium or barium was added to sulfuric acid solution of titanium to precipitate the corresponding sulfate, and the suspension was heated to hydrolyze the titanium chloride produced. For example, a solution prepared by dissolving hydrous titanic oxide in sulfuric acid and containing 15 per cent of the dioxide was treated with a chemically equivalent amount of a hot solution of calcium chloride and digested at 100° C. for 5 to 8 hours to carry the hydrolytic reaction to completion. A temperature just below the boiling point was employed to prevent decomposition of the iron chloride present. After thorough washing, the mixture was calcined to obtain a composite pigment containing 15 to 25 per cent titanium dioxide; most of the remainder was calcium sulfate. The precipitate appeared to be a coalescence of colloidal titanic acid and the alkaline earth sulfate particles.[7] According to a combination method, calcium chloride was added to the solution in smaller amount than that required to combine with all the titanium sulfate present, and, after separating this initial precipitate, barium chloride was added to the filtrate to complete the removal of sulfate, and the suspension was boiled to hydrolyze the titanic chloride. The washed

and calcined precipitate gave a soft white pigment containing 11 to 15 per cent titanium dioxide, 85 to 89 per cent barium sulfate, and less than 0.5 per cent ferric oxide.[8]

Stephens, Anderson, and Cash [9] reversed the procedure and added the titanium sulfate solution to a solution of an alkaline earth metal chloride (barium chloride, calcium chloride) at 30° to 35° C. to produce the extender in place, and heated the suspension at 100° C. to effect hydrolytic precipitation of titanic oxide on the particles of alkaline earth sulfate. The washed product was calcined to give a composite pigment of excellent properties. Extended pigments of higher purity were obtained by electrolyzing titanic sulfate solutions containing in suspension the desired proportion of particles of calcium sulfate, silica, barium sulfate, or china clay to reduce all the iron to the ferrous state and maintain a small proportion of titanous ions during the thermal hydrolysis.[10] The extenders were either added from an outside source or formed directly in the solution by introducing compounds such as calcium hydroxide or barium chloride, capable of forming insoluble compounds with the sulfuric acid present. Water was added to bring the titanium dioxide content to 3 per cent. To reduce the ferric component, the solution was electrolyzed between lead plates without a diaphragm, and heated at 90° to 95° C. with live steam to precipitate the titanium oxide, which deposited on and coalesced with the suspended material. The composite product was filtered, washed, and calcined at 700° to 800° C. to develop the desired pigment properties.

Such pigments were also produced by chemical precipitation of the extender in the acid liquor after hydrolysis of the titanium compound.[11] A sulfate solution of ilmenite was added to hot water containing a small proportion of a colloidal material, such as silicic acid, and the mixture was heated to complete the hydrolysis reaction. While the titanic oxide remained in suspension, a solution of an alkaline earth salt (barium chloride) was added to precipitate the corresponding sulfate by reaction with the liberated sulfuric acid, and the composite product was filtered, washed, treated with a borate, neutralized, and calcined. Better results were obtained by employing ilmenite solutions containing a slight amount of titanous salts and from which part of the ferrous sulfate had been removed by crystallization.

Von Bichowsky [12] produced a pigment of the substituted alkaline earth titanate type in which the alkaline earth oxide of the titanate was replaced by an alkaline earth sulfate such as barium sulfate or calcium sulfate. An equimolecular mixture of a titanium compound

(nitride) and an alkaline earth carbonate was heated with sulfuric acid in the amount theoretically required to form an acid salt. The reaction product was heated in water to obtain titanium dioxide and the sulfate of the alkaline earth metal. Carteret [13] precipitated hydrous titanic oxide on a suspended filler such as silicon dioxide, aluminum silicate, or kaolin. Fossil silica gave best results. The product was washed, dried, and calcined at a cherry red heat.

Barton [14] produced pigments of high opacity by suspending externally prepared extenders such as barytes, silica, china clay, and calcium sulfate in ilmenite solutions and heating the liquor to precipitate the titanium component. The two materials coalesced to produce a composite pigment characterized by particles of hydrous titanium oxide enclosed in and adhering to the filler (barium sulfate). The original solution prepared in the usual manner by digesting ilmenite with strong sulfuric acid was clarified and electrolyzed to reduce the iron component to the ferrous state before hydrolysis. Titanium oxide of pigment grade was obtained by hydrolytic precipitation from such solutions of specific gravity below 1.4, with free and combined acid concentration above 20 per cent, at temperatures below the boiling point. However, if the specific gravity was higher than 1.4 the acid was held below 20 per cent and the temperature below 100° C. Barium sulfate or calcium sulfate was used as carrier, and minute amounts of colloidal titanium compounds were added as nucleating agents.[15] In an example, a solution adjusted to 45 g. titanium dioxide and 50 g. sulfuric acid per liter, by adding dilute ammonium hydroxide to regular ilmenite solutions, was heated for 100 minutes at 90° C. to precipitate titanium hydroxide which was employed directly as nucleating agent.

An improved process involved the use of barium sulfate of special properties, chemically precipitated in a preliminary step by adding aqueous sodium sulfate to a solution of barium sulfide under controlled conditions.[16] The sulfide was obtained by roasting the mineral barite with powdered coal. This finely divided precipitate of barium sulfate was washed and added as a pulp to regular ilmenite solution in a proportion to give a pigment of the desired composition (25 to 30 per cent titanium dioxide and 70 to 75 per cent filler). After thorough mixing, the charge was boiled to effect hydrolytic precipitation of the titanium oxide, which as formed adhered to and coalesced with the extender particles. The product was filtered, washed, dried, and calcined to yield a composite pigment of exceptionally high hiding power. Similarly, a washed barium sulfate pulp precipitated from an acid medium was suspended in an ilmenite

solution and the titanium sulfate was decomposed by boiling the mixture.[17] The barium sulfate used in this case was prepared by adding to a suspension of finely divided barium carbonate in water containing about 0.1 per cent barium chloride an equivalent amount of sulfuric acid, with vigorous stirring. Alternatively, pure hydrous titanic oxide was added to the barium carbonate suspension before treatment with the acid.

Composite pigments containing high proportions of titanium dioxide (40 to 60 per cent) were prepared by a method similar to that used in producing the conventional lower strength products.[18] A paste of chemically precipitated barium sulfate was mixed with a sulfuric acid solution of ilmenite having a specific gravity of 1.5 and containing 6 to 12 per cent titanium dioxide and a small amount of free acid so as to obtain a complete suspension. All iron present was reduced to the ferrous condition. The proportions of constituents employed were such that the final product contained 50 per cent titanium dioxide and 50 per cent barium sulfate. After thorough mixing, the solution was heated either at atmospheric or autoclave pressure to effect hydrolysis of the titanium sulfate. The mixed precipitate was washed to remove iron salts and other undesirable impurities, and calcined to develop pigmentary properties. Buckman[19] hydrolytically precipitated titanic oxide on particles of barium sulfate suspended in the solution by heating the system at temperatures above 100° C. under a pressure greater than one atmosphere.

In producing an extended pigment of the conventional type, a slag was first made by fusing rutile or ilmenite with a barium compound, e.g., the carbonate and a reducing agent. In some cases fluorspar was added to the charge as a fluxing agent. The metallic iron was separated, and the paste of titanium and barium sulfates obtained by treating the slag with sulfuric acid was run into boiling water containing organic substances such as aldehydes, sugar, or starch to bring about hydrolysis.[20] The organic compounds were added to prevent iron salts, present as impurities, from coming down with the titanium. After reaction had gone to completion, the precipitate was washed, dried, calcined, and ground to yield a composite pigment of good quality. According to a modified process[21] the organic compound was suspended in the hot water into which the paste of barium and titanium sulfates was added, and it was converted to the sulfate by the acid liberated during the hydrolysis.[22]

Barton and Ryan found that a calcium sulfate composite pigment of high hiding power and better color could be made by employing hydrated calcium sulfate produced in a preliminary step under more

favorable conditions outside the ilmenite solution. This was accomplished by reaction between lime or calcium carbonate, as an aqueous slurry, and sulfuric acid, or by calcining natural or artificially prepared gypsum to destroy the original form, followed by milling and treatment with water to form a finely divided hydrated product. In preparing the chemically precipitated calcium sulfate, it was not essential that the reactants were pure, but better results were obtained by adding the lime slurry to the sulfuric acid in such proportions that the final liquor was somewhat acidic.

Seventy-five pounds of commercial lime was slaked in 500 pounds of water, and to the slurry, adjusted to 10 per cent solids, 135 pounds of 66° Bé sulfuric acid diluted with 500 pounds of water was slowly added in 1 hour, with constant agitation. During this time the temperature rose to 46° C. The charge was agitated for 1 hour to insure complete reaction, and then filtered to remove part of the acid liquor. In another example, 220 pounds of natural gypsum was milled to 33 mesh and heated at 110° to 120° C. for 3 hours. The material, then weighing 186 pounds, was added to 400 pounds of cold water and agitated for one half hour to ensure reformation of the dihydrate.

The clarified and reduced ilmenite solution employed contained 5.73 per cent titanic oxide, 4.80 per cent ferrous oxide as sulfates, and 22.45 per cent sulfuric anhydride. To 1100 pounds of this liquor was added 560 pounds of pulp containing 220 pounds of dehydrated calcium sulfate, followed by 350 pounds of water, and the charge was boiled with continuous agitation until 95 per cent of the titanium had been precipitated hydrolytically. This required about 5 hours. The slurry was then diluted with an equal volume of water, allowed to settle, and the clear supernatant liquor was decanted. After separation of the acid liquor, the precipitate was filtered, washed, and calcined at 900° C. for 2 hours to produce a pigment containing 29.4 per cent titanium dioxide and 70.6 per cent calcium sulfate.

Calcium sulfate prepared in this manner was characterized by acicular crystals of great length in proportion to their other dimensions. It offered a large surface for adsorption of the titanic oxide as precipitated, and permitted a more complete removal of iron salts by washing. Such factors as concentration, acidity of the solution during hydrolysis, and calcination temperature could be varied within wide limits, depending upon the results desired.

Preformed calcium sulfate of acicular shape, prepared by precipitation in acid or alkaline media or by calcination of natural or by-product gypsum, gave improved pigments.[23] Such material was

suspended in ilmenite solution and the mixture was heated to effect hydrolysis. The composite precipitate was washed, neutralized, treated with a small proportion of phosphoric acid, and calcined to produce a pigment consisting of 30 per cent titanium dioxide and 70 per cent of the extender. This method was also applicable to composites containing relatively high proportions of titanium dioxide.[24] Acicular calcium sulfate was suspended in sulfuric acid solution of ilmenite containing 6 to 12 per cent titanium dioxide in such amounts that the final precipitate, after boiling to hydrolyze the titanium sulfate, contained approximately 50 per cent of the extender. The pulp was washed, treated with a small proportion of an alkali metal salt (potassium sulfate), and calcined at 800° to 1000° C.

Washburn and Aagaard [25] prepared a pigment of greatly improved properties by chemically precipitating the calcium sulfate separately and converting it to the anhydrite form before mixing it with the ilmenite solution. The use of hydrated calcium sulfate (gypsum) offered several objections. For instance, the opacity or covering power of the composite product per unit of titanium dioxide fell off rapidly as the percentage of gypsum increased; similarly, the color of the pigment became poorer with increasing proportions of titanium dioxide. Both these difficulties were probably due to the limit in the capacity of the suspended calcium sulfate, of gypsum form, to absorb the hydrous titanium oxide precipitated during hydrolysis. The acicular particles were not only relatively large initially, but were also somewhat unstable. They tended to grow in size during processing, with the result that they had a tendency to occlude iron and other discoloring impurities present in the solution.

Dehydrated calcium sulfate was prepared by adding a slurry of hydrated lime or calcium carbonate to concentrated sulfuric acid under controlled conditions of concentration, temperature, and time of heating to produce an extremely finely divided product having the anhydrite structure. As a result of this extreme state of subdivision, each unit of weight of the extender supplied more particles and much more surface to act as adsorption nuclei for the precipitated compounds of titanium. This not only resulted in an accelerated rate of hydrolysis, but also yielded pigments of superior color and covering power, even with higher proportions of titanium dioxide. Considerable heat was evolved by the reaction between the lime and sulfuric acid, and this was conserved by adding the hot suspension to the ilmenite solution. The mixture was further heated to effect hydrolysis, and the titanium compounds, on precipitation,

largely coalesced with the calcium sulfate and the two components could be present in any proportions, whereas former methods were only applicable to composites containing relatively low proportions of titanium dioxide. The coalesced precipitate was washed and calcined at 900° to 1000° C.

In an actual operation, ilmenite ore was brought into solution after digestion with strong sulfuric acid; all the ferric iron and a small part of the titanium were reduced to their next lower valences by introducing metallic iron, and the residue was allowed to settle after coagulation with glue. A slurry of 95 pounds hydrated lime in 110 gallons of water at 70° C. was added slowly, with agitation, to 372 pounds of 78 per cent sulfuric acid at 20° C. Considerable heat was evolved by the reaction, and the resulting suspension of calcium sulfate in dilute sulfuric acid (2 to 5 per cent) was further heated near the boiling point to effect practically complete dehydration. To this thick pulp of anhydrite, in the tank in which it was formed, was added 900 pounds of the clear supernatant ilmenite liquor containing 7.02 per cent titanium dioxide, 6.85 per cent ferrous oxide as sulfates, and 2.26 per cent uncombined (free) sulfuric acid. The mixture was then heated to boiling and maintained until 95 per cent of the titanium was hydrolyzed, after which the composite precipitate was washed, dried, and calcined at 900° C. to yield a pigment containing 29.6 per cent titanium dioxide and 70.3 per cent calcium sulfate, with only traces of other substances. The effective specific gravity was 3.2.

In another example, to 106 pounds of 78 per cent sulfuric acid at 20° C., in a lead lined tank, was added slowly, with agitation, a slurry of 39 pounds hydrated lime in 44 gallons of water at 70° C. With these proportions the resulting liquor was slightly acid. After the calcium sulfate had been converted to the anhydrite form, 2600 pounds of reduced and clarified ilmenite solution containing 6.07 per cent titanium dioxide and 5.88 per cent ferrous oxide as sulfates and 6.45 per cent uncombined sulfuric acid was added. The mixture was boiled to effect hydrolysis of the titanium sulfate, and the combined precipitate was washed and calcined as before to produce a pigment containing 74.4 per cent titanium dioxide, 25.2 per cent calcium sulfate, and traces of other components.

This process was also applicable to the manufacture of composite pigments consisting of titanium dioxide, calcium sulfate, and other extenders, such as barium sulfate and silica.[26] In preparing such products containing relatively low percentages of titanium dioxide, up to about 35 per cent, the extender material normally furnished

sufficient absorption centers for the hydrolytic precipitation, but there was a limit to its capacity to function in this manner. The addition of calcium sulfate made it possible to produce pigments above this range, having excellent properties. As before, the calcium sulfate was prepared under such conditions of concentration and temperature that it was very finely divided and had the structure of anhydrite. In this form it accelerated the hydrolytic decomposition of titanic sulfate to a much greater extent than the ordinary relatively insoluble extenders.

A slurry of 25 pounds hydrated lime in 28 gallons of water at 70° C. was added, with agitation, to 150 pounds of 78 per cent sulfuric acid at 20° C. so as to produce the anhydrite form of calcium sulfate. The resulting slurry was mixed with 25 pounds barium sulfate and 1300 pounds of an ilmenite solution containing 6.07 per cent titanium dioxide, 5.88 per cent ferrous oxide as sulfates, and 6.45 per cent uncombined sulfuric acid. Live steam was then injected and the charge was boiled until 95 per cent of the titanium sulfate was hydrolyzed. The composite precipitate was separated, washed free of calcium sulfate, dried, and calcined at 900° C. to produce a pigment containing 74.8 per cent titanium dioxide, 25.1 per cent barium sulfate, and traces of other substances. Calcium sulfate was removed from the mixed precipitate by washing, because of the greater relative solubility in water.

Ryan and Cauwenberg [27] effected the hydrolytic decomposition of titanic sulfate solutions in the presence of finely divided natural calcium sulfate instead of the chemically precipitated product. The mineral gypsum was wet-milled in the presence of added substances to reduce its solubility in water and retard its crystal growth, e.g., calcium hydroxide, sodium sulfate, glue, gelatin, and gum arabic. Any iron present as impurity was converted to the soluble ferrous state by adding sodium sulfite, sodium thiosulfate, or a similar reagent. The slurry was then neutralized with hot dilute sulfuric acid and added to a hot ilmenite solution. After adjusting the concentration of sulfuric acid, free and combined, to 12 per cent, the mixture was boiled to effect hydrolysis of the titanium sulfate and the combined precipitate was filtered, washed, dried, and calcined at 900° C. to produce a composite pigment of superior properties.

The rate of hydrolysis was accelerated, and at the same time a product of improved pigment properties was obtained, by heating ilmenite solution previously seeded with alkali-precipitated titanic acid and carrying in suspension particles of calcium sulfate of anhydrite form.

Composites of improved properties were obtained by adding the titanium sulfate solution to an aqueous suspension of calcium sulfate at such a rate that the mixture was complete in 1 to 3 minutes.[28] The solution was heated immediately to boiling to effect hydrolysis. Composite pigments were obtained by thermal hydrolysis of sulfate solutions of ilmenite in the presence of an extender such as barium sulfate and calcium sulfate, after nucleating with gamma titanic acid [29] or a composition obtained by heat-treating a dispersion of gamma titanic acid in aqueous sulfuric acid.[30] McCord and Saunders [31] suspended a calcium sulfate extender and gamma titanic acid in dilute sulfuric acid solution and boiled the slurry with agitation. The mixed precipitate was filtered, washed, and calcined to develop pigment properties.

The color, brightness, and covering power of composite pigments having an alkaline earth metal sulfate base were improved by adding boric acid or a borate, such as that of calcium or barium, to the washed pulp before calcination.[32] Calcium hydroxide or barium carbonate was added to the washed coalesced precipitate to neutralize all residual sulfuric acid and render the product slightly alkaline. Calcium or barium borate in the proportion of 2 to 4 parts per 100 parts of titanium was intimately distributed through the mass by agitation or by boiling. The mixture was dewatered and calcined at 700° to 900° C. Better results were obtained by seeding the ilmenite solution before mixing it with the extender material.[33] This is a modification of a process developed for producing relatively pure titanium dioxide of pigment grade. An extremely fine and effective calcium sulfate having the anhydrite structure was obtained by adding a slurry of lime or calcium carbonate to concentrated sulfuric acid under controlled conditions of concentration and temperature.

Hydrous titanium oxide nuclei were precipitated by carefully pouring a solution of 8.6 kg. potassium carbonate into 26 liters of water at 80° C., upon the surface of 745 kg. of ilmenite solution containing 6 per cent titanium dioxide. The precipitate was stirred immediately into the solution, the liquor was added gradually to a slurry of anhydrite in such proportions as to give a final pigment of the desired concentration, and the mixture was boiled to effect hydrolysis. In preparing other composites as the barium sulfate base product, a small amount of calcium sulfate was included in the charge to insure best results.

Rutile-type pigments were produced by calcining at 750° to 1000° C. the hydrolysis product obtained by boiling a sulfuric acid solution

of ilmenite containing a suspension of an activated anhydrite form of calcium sulfate.[34] In a related process, a nucleating agent prepared by the thermal hydrolysis of titanium fluoride was added to the suspension of extender in sulfate solution of ilmenite before hydrolytic precipitation of the titanium.[35]

Calcium sulfate and barium sulfate extended pigments in which the titanium dioxide component was in the rutile crystal modification were obtained by treating the regular coalesced product with a small proportion of zinc oxide or other zinc compound before calcination.[36] Hydrous titanic oxide was coprecipitated from a sulfuric acid solution of ilmenite on a calcium sulfate or barium sulfate extender, so that the final pigment contained 30 per cent titanium dioxide. After thorough washing, 1 per cent zinc oxide was added and the mixture was calcined at 775° to 1000° C. Such pigments were characterized by improved resistance to chalking and high tinting strength characteristic of rutile. High resistance to chalking was developed by continuing the normal calcination period or by raising the temperature, but at the expense of tinting strength. The desired balance of properties was obtained by regulating the degree of calcination. Stark [37] prepared a composite rutile-barium sulfate pigment by treating pure titanium sulfate solution, obtained by dissolving hydrolytically precipitated titanic acid in strong sulfuric acid, with barium nitrate to precipitate the barium sulfate extender and convert the solution to nitrate. A nucleating agent was added and the solution was boiled to effect hydrolysis. The precipitate was filtered, washed, and calcined to develop its pigment properties.

Blended Composites

Barton [38] blended mineral fillers having relatively low indices of refraction (barium sulfate, silica, gypsum, clay, and asbestine) with pigments consisting of titanium dioxide alone or coalesced with alkaline earth metal sulfates by grinding the constituents together in the dry state. The proportion of intermixed mineral extender was not more than 20 per cent of the total weight.

A composite pigment in which the extender particles were coated with very finely divided titanium dioxide was prepared by coagulating an aqueous dispersion of the uncalcined product obtained by thermal hydrolysis of ilmenite solutions.[39] Hydrous titanic oxide precipitated in this manner retained from 3 to 8 per cent closely held sulfuric acid which was removed before colloidal dispersion was effected. This was conveniently accomplished by washing the

material first with an alkaline solution to ·neutralize the residual acid, and then with water to remove the salts formed by the neutralization. Hydrochloric, nitric, and hydrobromic acids acted as efficient peptizing agents. To one part of neutralized and washed titanium dioxide in the form of a filter cake containing 60 per cent water was added 0.06 part of hydrochloric acid, with stirring, and as a result of conversion to the colloidally dispersed or peptized form the system became quite fluid. The desired amount of extender, such as alkaline earth metal sulfates of pigment grade, was added to the peptized solution either in the dry form or as a separate aqueous suspension. More water was added if necessary, since the colloidal character of the titanium dioxide was independent of dilution. After thoroughly mixing the components, the titanic oxide was thrown out of the colloidally dispersed state and caused to coagulate on the extender particles. This was conveniently accomplished by adding polybasic acids or their soluble salts, such as phosphoric acid and magnesium sulfate, or by neutralizing the peptizing acid with ammonium hydroxide, sodium carbonate, or other alkali. During this step the mixture was agitated constantly to ensure an even disposition of the coagulated particles on the extenders, and the composite product was filtered, washed, calcined, and pulverized.

In an example, a peptized solution containing 1200 g. titanium dioxide dispersed in 2500 g. of water with 70 g. hydrochloric acid was diluted with an equal volume of water. Five thousand grams of blanc fixe was gradually added, with stirring, and 50 g. magnesium sulfate was introduced. The latter compound caused the peptized titanium dioxide to be thrown out of dispersion and to coagulate on the secondary pigment particles. Stirring was continued for one-half hour, after which the slurry was put through a filter press and the precipitate was washed, dried, calcined, and pulverized to obtain a composite pigment containing 20 per cent titanium dioxide in the form of extremely small particles.

According to a related process,[40] barium sulfate was added to or formed in a fine dispersion of titanium dioxide which was then coagulated by adding barium carbonate. Peptization was accomplished by agitating the titanic oxide in water containing a small proportion of hydrochloric or nitric acid, barium or strontium chloride, or nitrate. The barium carbonate effected coagulation by neutralizing the acid, however, employing the neutral dispersing agent; salts of polybasic acids, as magnesium sulfate, were employed as precipitants.

Alcock and Weber [41] mixed three parts of hydrolytically precipitated titanium dioxide with seven parts of blanc fixe, both as pastes in water, by stirring or by agitation. The carefully blended product was dewatered and heated to 650° C. Pigments having better properties were obtained by adding a small proportion of a carbonaceous material, such as starch, sugar, oil, or charcoal, to the blended paste and calcining at 700° to 950° C. until all carbon was burned out. Similarly, iron-free titanium hydroxide was mixed with a filler in the wet state; 8 per cent sawdust or other carbonaceous material was incorporated, and the composition was calcined at 800° C. to develop the desired pigmentary properties. [42]

Hydrous titanium oxide obtained by the thermal hydrolysis of a sulfate solution of ilmenite was mechanically mixed with an inert extender such as barytes, gypsum, blanc fixe, China clay, alumina, and silica, and treated with barium chloride, sodium hydroxide, barium hydroxide, calcium chloride, calcium carbonate, or lime to neutralize or replace the closely held acid. The product was then washed to remove all soluble compounds and calcined to produce a composite pigment. A small amount of phosphoric acid or a fusible phosphate added just before calcination improved the pigmentary properties. Alternatively, the titanium oxide pulp was treated to neutralize the acid, and washed free of soluble salts before mixing with the inert material. [43]

Alessandroni [44] prepared composites of this type by coflocculating aqueous dispersions of the components without addition of coagulants. One hundred pounds of calcined titanium dioxide of pigment grade was ground for 2 hours in a ball mill with an equal weight of water and 1 per cent of its weight of aluminum chloride. Another suspension was prepared by ball-milling 300 pounds of ground, purified, bleached, and elutriated barytes or chemically precipitated barium sulfate for 2 hours with an equal weight of water and 0.50 to 0.75 per cent of sodium silicate having a ratio of sodium oxide to silica of 1 to 4. The two dispersions were then mixed in a suitable tank and mutual coflocculation resulted through interaction of the aluminum chloride and sodium silicate. The coflocculated, integrated pigment particles were separated from the supernatant liquor, washed, dried at 100° to 120° C., and pulverized. According to another modification, 100 pounds of calcined titanium dioxide was milled for 2 hours with an equal weight of water containing 4.5 pounds of sodium silicate. Similarly, 300 pounds of pigment-grade barium sulfate was dispersed separately by milling for 2 hours in an equal weight of water with 9 pounds of sodium silicate, and the two

suspensions were brought together. Since the same dispersing agent was used for both primary and secondary pigments, no coagulation occurred, and 2.4 pounds of magnesium sulfate dissolved in water was added to bring about a coflocculation and integration of the components. This method was reported to be applicable to three-component pigments, for example, titanium dioxide, barium sulfate, and lead carbonate. Among the agents which exerted a dispersing effect on the various pigments were carbonates and hydroxides of alkali metals; alkali metal silicates; acidic halides of tri- and tetra-valent elements such as titanium, aluminum, zirconium, and thallium; certain inorganic salts, such as lead chloride and barium chloride; sodium hexametaphosphate; and a number of organic compounds.

In a related process, particles of titanium dioxide and barium sulfate were dispersed in a single aqueous medium with a small proportion of casein, and sulfuric acid was added to bring about coagulation.[45] The coflocculated composite pigment was filtered, washed, dried, and disintegrated.

Titanium oxide was peptized with sulfamic, chloric, bromic, iodic, perchloric, perbromic, or periodic acid or their barium salts, and the resulting colloidal suspension was subsequently coagulated by decomposing the agent on heating the system above 80° C.[46] Sulfamic acid and its barium salt gave best results, and at the temperature employed the agent decomposed into ammonium bisulfate which served as a coagulant. Washed hydrolysis pulp was first transformed to colloidal suspension by these agents, extenders such as barium sulfate or calcium sulfate were thoroughly mixed in, and the system was heated to effect coagulation. The mixed precipitate was filtered, washed, and calcined at 900° C. According to a specific operation, washed filter cake containing 8 parts sulfuric acid per 100 parts of titanium dioxide was treated with aqueous barium sulfamate in an amount sufficient to precipitate all the sulfuric acid as blanc fixe. Two hundred and fourteen parts of separately prepared barium sulfate was added, and the uniform dispersion of the two components was heated to boiling to effect coagulation. The composite precipitate was washed and calcined at 900° C. to produce a pigment of 30 per cent titanium dioxide and 70 per cent barium sulfate. Calcium sulfate extended pigments were produced in the same manner.

Booge [47] made blended pigments in which the individual particles of titanium dioxide and extender (barium sulfate or calcium sulfate) existed independently side by side by mechanically mixing selected components of specific particle size. These blends, although

physically different, were equal and within certain limits of composition superior in hiding power, tinting strength, brightness, and reflectance to coalesced pigments having the same components in the same proportions.

Ordinary barium and calcium sulfates, as commercially available or as made by standard processes, gave unsatisfactory blends. Such products were inferior in color, tinting strength, and hiding power to corresponding amounts of titanium dioxide alone, whereas compositions in which the same amounts of components were coalesced were equal or slightly superior to the same amount of the straight oxide. So in order to obtain alkaline earth metal sulfates having the desired properties, new methods and treatments and modifications of existing processes of manufacture were devised.

Titanium dioxide for blending was of pigment grade with a hiding power of at least 90 square centimeters per gram and it had a frequency particle size of not more than 0.5 micron. At least 90 per cent of the particles were not greater than 1.5 microns. (It was of crystalline nature such as that developed by calcining hydrous titanium oxide obtained by hydrolytic precipitation.) Naturally, a product of good color and brightness was selected; the reflectance was 0.94 or higher.

The alkaline earth metal sulfates had a frequency particle size average of not more than 0.75 micron, and at least 90 per cent of these particles were below 1.5 microns. These sulfates had such low hiding power and tinting strength that these properties were practically immaterial in respect to pigment properties of the blends. They were of good color, however, and had a reflectance in the blue region of at least 0.94 and preferably 0.975.

Hiding power of such blended pigments, containing 20 to 40 per cent titanium dioxide, was appreciably greater than that of equivalent coalesced products and of straight titanium dioxide but fell off beyond this range. This characteristic was particularly noticeable in the barium sulfate base blends. Calcined titanium dioxide sometimes had a yellowish tone, and to counteract this an alkaline earth metal sulfate of higher reflectance was employed. For instance, a reflectance of 0.975 safely took care of any slight yellowish cast of ordinary intensity.

The oil absorption of alkaline earth sulfate-titanium dioxide pigments in general varies inversely with the temperature at which calcination is effected. For coalesced products a very high temperature is required by the titanium dioxide component for development of its full pigment properties, and the resulting oil absorption

cannot be changed greatly except that the value may be reduced by an additional dry-milling step. On the other hand, blends of similar composition may be produced having an oil absorption such as is required for practical paint use, since the titanium dioxide is calcined before mixing. Thus high oil absorption may be obtained by blending alkaline earth metal sulfates which have been heated at temperatures below 500° C. if at all, while lower values can be obtained by employing sulfates which have been subjected to temperatures above 500° C. Usually it is more convenient to calcine the mixture of alkaline earth sulfate and precalcined titanium dioxide at the temperature at which the desired oil absorption is developed. Values from 39 to 14 may be obtained in calcium sulfate base pigments.

Within the limits of 15 to 30 per cent titanium dioxide, the alkaline earth metal sulfates act as reinforcing pigments in the blends, whereas such sulfates of a coarser particle size act merely as inert diluents and may even decrease the pigmenting value of the added titanium dioxide. Fortunately, within this range are to be found the most practical and useful pigments of the type. Below 15 per cent the strength and hiding power of such pigments are too low to warrant the use of a comparatively expensive titanium dioxide component. Similarly, above 35 per cent the bulking value becomes too low and the cost too high to compete with other comparable white pigments such as lithopone. For example, if an extended pigment of higher titanium dioxide content is used in a paint, the amount required for satisfactory hiding power is not sufficient to impart the necessary body or consistency required for good brushing out and other practical application properties.

Any desired method of blending the constituents can be followed so long as a most thorough distribution of one component throughout the mass of the other is obtained. Although this can be accomplished in the dry state, in general wet blending is more convenient to carry out. Aqueous pastes of the pigment-grade titanium dioxide and of the alkaline earth metal sulfate were mixed and thoroughly agitated for several hours until the individual particles were completely dispersed and thoroughly blended. The mixture was then filtered, dried, and in some cases recalcined, and disintegrated. If desired, the product was subjected to a controlled dry-milling process to reduce the oil absorption. Such grinding did not reduce the particle size of the components, however, and the lowering of oil absorption value was caused by some change in surface or adsorption characteristics of the particles.

For example, a slurry of barium sulfate precipitated from barium chloride with sulfuric acid was mixed with a slurry of pigment-grade titanium dioxide. Barium hydroxide was then added in an amount equal to 3 ml. of a one-fiftieth normal solution for each 20 g. of finished pigment to produce a slight alkalinity. The mixture was agitated for 24 hours, filtered, dried, and disintegrated.

In preparing titanium dioxide of the required quality, the hydrous oxide precipitated by thermal hydrolysis of ilmenite, according to the method of Blumenfeld, was washed with water to remove sulfuric acid, iron compounds, and other impurities not firmly adsorbed, treated with a potassium compound, and calcined at 950° C., according to conventional methods. The pigment was then wet ground, dispersed, hydroseparated, coagulated, and settled, according to the accepted practice, to obtain a pulp suitable for wet blending directly, or if desired the mass was dried and ground before mixing with the other components.

Several processes have been developed for producing barium and calcium sulfates of the required properties. In preparing barium sulfate by precipitation from chloride solutions with sulfuric acid, specific conditions were maintained to develop the proper characteristics. Particle size was largely influenced by the temperature at precipitation as well as by the concentration of the solutions. The reflectance and color were influenced by the precipitation conditions, primarily by the purity of the solutions employed. Oil absorption somewhat paralleled the particle size in being influenced by concentration and temperature at precipitation.

The barium chloride solution was first purified by adjusting the hydrogen ion concentration to a pH of 8 to 9, oxidizing any iron present, and filtering off the precipitate. Concentrations of 50 to 60 g. barium per liter and sulfuric acid of 60° to 65 ° Bé gave best results. By carrying out the precipitation at a low temperature, for instance near the freezing point, extremely fine barium sulfate having a frequency particle size average of around 0.2 micron was produced. At room temperature a product of relatively high oil absorption resulted. From room temperature to about 65° C. the blanc fixe of a frequency particle size average of 0.40 to 0.75 micron was obtained, and this product was pre-eminently suited for use in blends intended for outside paints. At temperatures above 65° C. and at other concentrations, the particles become too coarse and the resulting pigments were of lower tinting strength and hiding power. With a slurry of 80 g. to 100 g. barium sulfate as a standard, within reasonable limits, a product of similar particle size was formed if for

each 10° C. change in precipitation temperature the concentration was changed by 20 g. per liter barium sulfate in the opposite direction; that is, an increase in temperature was compensated by a decrease in concentration.

As an example, 275 liters of a solution containing 85 g. barium chloride per liter was purified by adjusting the pH to 8 and filtering. The filtrate was run into a wooden tank fitted with a wooden agitator and a rubber steam inlet, and live steam was injected to raise the temperature to 50° C. A slight excess of 66° Bé sulfuric acid at 25° C. was added, with constant agitation, over a period of 15 minutes, and during this period the temperature rose to 60° C. The precipitate was freed from mother liquor and adhering impurities by several filtering and repulping operations and was finally adjusted to neutrality. This product had a frequency particle size average between 0.50 and 0.75 micron, and more than 90 per cent of the particles were not larger than 1.5 microns.

In producing a still finer material, 275 liters of the purified barium chloride solution was cooled to 8° C., and a slight excess of 66° Bé sulfuric acid at 25° C. was added simultaneously with cracked ice in such proportion that the temperature did not exceed 10° C. The resulting barium sulfate, after treatment as before, had a frequency particle size average of 0.2 to 0.3 micron, with at least 90 per cent below 1.5 microns. This product, on blending with titanium dioxide, gave a pigment of somewhat higher oil absorption and tinting strength than the slightly coarser barium sulfate precipitated at 50° to 60° C.

Blanc fixe of the specified properties was also obtained by double decomposition reaction between barium sulfide and alkali metal sulfates, provided that concentrations of solutions, temperature, and manner of precipitation were carefully controlled. Any residual sulfides proved especially injurious in paints, and to remove these objectionable impurities completely, the blanc fixe was washed with an acid solution, calcined, and rewashed with the acid solution.

To illustrate, a barium sulfide solution of 30° Bé was filtered to remove all suspended matter and heated to 80° C. A second solution, containing 230 g. sodium sulfate per liter, was heated to 35° C. and the two were added simultaneously to a precipitation tank at such rates as to maintain at all times a slight excess of soluble sulfate. Constant agitation was maintained. Because of strong adsorption of sulfides, a small proportion remained with the precipitate even after prolonged washing with water. After reducing the sulfide

content to a minimum, however, the cake was repulped in water to a slurry containing 33 per cent solids, and sulfuric acid was added to bring the pH to 2. The treated product was again washed with water until the supernatant liquor had a pH of 3 to 4. Dilute alkali was then added to bring the pH to 7 or 8, and the pulp was filtered, dried, and calcined at 500° C. in an oxidizing atmosphere. Another slurry containing 33 per cent solids, obtained by discharging the hot blanc fixe in water, was given a second acid treatment identical with that employed before calcination, and was finally adjusted to neutrality with dilute alkali.

This product possessed a frequency particle size average below 0.75 micron, and less than 10 per cent of the particles were above 1.75 microns. It was free from sulfides; had an especially good color; and oil absorption was within the desired range. Blends with titanium dioxide possessed tinting strengths and hiding power equal to or better than coalesced pigments of the same chemical composition.

Calcium sulfate of the anhydrite form having pigmentary properties within the specific limits were produced easily by chemical precipitation. For example, a slurry containing 200 g. slaked lime per liter was gradually added to 60° Bé sulfuric acid until 85 per cent of the acid was neutralized. During the initial stages of the precipitation the temperature rose rapidly to approximately 113° C., then fell off slowly. The reaction mass was held close to the boiling point, with thorough agitation, until a very few acicular crystals (gypsum) remained, as determined by observation under a microscope at 400 magnifications. The slurry of anhydrite was then filtered and washed until the filtrate showed a pH of at least 4. The cake was repulped in fresh water made alkaline by adding a small amount of sodium hydroxide, and again filtered. This product was blended with titanium dioxide without further treatment or after calcination. Since the presence of alkali metal compounds during calcination lowered the oil absorption of the product, traces of sodium hydroxide remaining with the calcium sulfate had such an effect. A product of excellent color, and a frequency particle size average of 0.5 micron with more than 90 per cent of the particles below 1.5 microns, was obtained.

Calcium sulfate produced in this manner may be calcined separately and then mechanically mixed with titanium dioxide of specified properties, or, for the sake of simplicity and ease of large-scale operation, the two components may be blended prior to calcination of the calcium sulfate.

In the preparation of calcium sulfate for composite titanium dioxide pigments, milk of lime is reacted with strong sulfuric acid. The precipitate is separated from the mother liquor, washed, and treated with an alkaline solution to neutralize the last traces of residual acid so that the calcined material will have a neutral reaction. Milk of lime prepared by the conventional methods, however, contains relatively coarse particles of crystalline hydrated calcium hydroxide which are not attacked to an appreciable extent by sulfuric acid, and thus they appear in the final product as "alkaline spots." On calcination, these particles are converted to the oxide, and they may react with other constituents to form gritty products. Elimination of the crystalline hydrate may be effected by preparing the milk of lime within a narrow range of temperature,[48] 68° to 78° C., and at no time during or after hydration should the lower limit of 50° C. or the upper limit of 85° C. be passed for a protracted period of time. Higher temperatures accelerate the formation of nonreactive crystalline particles, while at lower values hydration is slow and incomplete. For economic measures the milk of lime should be as concentrated as can be handled practically by standard pumps and equipment, and 15 to 20 per cent calcium oxide has proved most satisfactory. Such a slurry is reacted with 75 to 80 per cent sulfuric acid to form the calcium sulfate.

In a typical operation, 500 gallons of water at 40° C. was run into a tank and pebble lime was then added at the rate of 100 pounds per minute for a period of 5 minutes. As the hydration reaction proceeded, the temperature rose rapidly to 80° C., and at this stage water at 18° to 20° C. was introduced continuously at a rate of 75 gallons per minute. The temperature of the slurry dropped to 68° to 78° C. More quicklime was fed in continuously with the cold water at such a rate as to maintain the required consistency and temperature range of the overflow. After 1 hour the operation was discontinued, the tank was emptied and flushed, and the procedure was repeated.

The initial high temperature of 80° to 85° C. prevented incomplete hydration at the beginning and was not objectionable, since it was maintained for only a short period of time. After 1 hour the operation was discontinued, the tanks were emptied and washed, and the entire procedure was repeated to avoid formation of crystalline hydrate which would result from long and continuous operation even within the optimum temperature range. In general, the temperature of the water in the tank at the beginning of the reaction was between 30° and 35° C., and of the water added later between 15° and 25° C.

Stable, finely divided, insoluble anhydrite having nonacicular crystal form was prepared from chemically precipitated calcium sulfate containing less than 6.2 per cent combined water by digesting at an elevated temperature in a dilute aqueous solution of sulfuric acid of not more than 15 per cent concentration.[49] Sullivan [50] prepared anhydrite of the required grade by adding a slurry of lime or calcium carbonate to strong sulfuric acid. However, after 75 per cent or more of the acid had been neutralized a solid reaction product containing an appreciable amount of hydrated calcium sulfate suspended in the liquor was obtained. By heating it for 1 hour at 80° to 100° C., this component was then converted to the desired anhydrite form suspended in an aqueous acid medium containing from 1.5 g. to 150 g. per liter sulfuric acid.

Calcium sulfate having improved pigment properties and particles of specific size and shape was obtained by hydrating the regular chemically precipitated anhydrite, subjecting it to strong shearing action, and then dehydrating the ground material.[51] The shearing action was accomplished in a kneading machine, or in a ball, pebble, roller, or stone mill. The same treatment was applicable to calcium sulfate associated with titanium dioxide as employed in producing blending pigments.[52] Calcium sulfate containing less water than the dihydrate was hydrated in the presence of aqueous suspensions of titanium dioxide pigment, and the mix was concurrently subjected to a mechanical shearing action, as before, and the product thus obtained was dehydrated within 30 minutes after the previous treatment. The shearing forces broke down larger particles and prevented crystal growth during the hydration. Such a mixture, dried at 65° C. or less, gave a pigment consisting of titanium dioxide and gypsum, the average particle size of the latter being 1 to 3 microns. If calcined at 600° to 900° C., the calcium sulfate component was in the form of insoluble, nonacicular anhydrite having a uniform particle size of about 1 micron. Mixing of the titanium dioxide and calcium sulfate was carried out effectively in a Banbury mixer or a ball mill.

Anhydrite prepared in contact with sulfuric acid tended to become hydrated and increase in particle size on standing in aqueous media. At room temperature this change took place even in 16 per cent sulfuric acid.[53] However, such a product was made resistant to hydration and increase in particle size while stored as an aqueous suspension by adding a solution of a protein, such as glue, having a pH not less than 4 [54] or by admixing 0.10 to 1 per cent of a water-soluble glycolate such as an alkali metal starch glycolate.[55]

In an acid process for producing barium sulfate of pigment grade, finely ground barytes was heated to a temperature above 50° C. with 2 parts, by weight, of 93 per cent or stronger sulfuric acid to produce a reaction product consisting essentially of $BaSO_4 \cdot H_2SO_4$. This material, suspended in the excess acid, was diluted with water at a temperature of at least 50° C. to precipitate the barium sulfate in a finely divided form which was filtered and washed.[56]

A composite pigment of low oil absorption was prepared by pulverizing a dry mechanical mixture of calcined titanium dioxide and calcined calcium sulfate in a mill of the ring-roll type.[57]

Nichols [58] produced noncoalesced composites by mixing titanium dioxide or a white insoluble titanate with an extender having an index of refraction less than 1.44, such as fluorides of sodium, magnesium, calcium, sodium-aluminum, magnesium-silicon, and sodium-calcium-aluminum. Such blends in nonaqueous form had greater hiding power than similar products in which extenders having indices of refraction greater than 1.44 were employed. Blends containing 5 per cent silica were reported to possess the covering power and other pigmentary properties of pure titanium dioxide.[59] Silica of the proper texture was prepared by calcining the precipitate obtained by treating the solution of an alkali metal fluosilicate with ammonium hydroxide.

A composite of considerable commercial importance is produced by carefully blending 30 parts by weight of finished titanium dioxide pigment with 70 parts of a selected and treated magnesium silicate extender. Any convenient method of mixing may be employed, although this may be accomplished effectively in the dry state by grinding the components together in a mill of the ring-roll type.

Barton [60] treated a calcium sulfate base, composite with an aqueous solution of alkali metal carbonates (sodium carbonate), which reacted to form a soluble sulfate and calcium carbonate. The precipitate was filtered, washed, dried, and pulverized. Such products had greater apparent density, lower oil absorption, and greater hiding power than similar compositions prepared before, as, for example, by blending the components. Regardless of its crystalline condition, calcium carbonate obtained in this manner had an external form pseudomorphic after the original calcium sulfate, and thus possessed the same particle size and shape.

In a typical operation, the starting material was a coalesced pigment containing 30.4 per cent titanium dioxide and 69.6 per cent calcium sulfate, with a dry color equal to the 1 standard, an oil absorption of 21.2, and tinting strength of 460 or 15.1 per unit of

titanium dioxide. Five hundred parts, by weight, of this material was slurried in a solution of 272 parts of soda ash in 2000 parts of water, and the mixture was allowed to stand, with occasional stirring, for 24 hours at room temperature (20° C.). The new product was filtered, washed, and dried at 100° C. to yield 408 parts of a pigment containing 37.6 per cent titanium dioxide and 61.8 per cent calcium carbonate. It had a dry color equal to the 1 standard, an oil absorption of 23.5, and a tinting strength of 580 or 15.5 per unit of titanium dioxide. The oil absorption of the product was reduced to 16.3 by milling in a chaser mill.

Crundall [61] precipitated hydrous basic titanium phosphate from sulfate solutions by adding phosphoric acid or a soluble phosphate. By carrying out the reaction in the presence of suspended barium sulfate, composite pigments were obtained. Mixtures suitable for use as pigments were obtained by treating basic titanic phosphate with alkaline oxides, hydroxides, or carbonates. [62] Barium sulfate and compounds of iron and chromium were incorporated to obtain white or colored products.

Other composites were prepared by blending with titanium dioxide of pigment grade precipitated barium carbonate [63] which had been calcined at 200° to 600° C. to increase the particle size, and with diatomaceous earth. [64] Turbett and Vahrenkamp [65] formed a composite pigment for outdoor use by treating fused lead silicate with water and grinding the hydrated product with titanium dioxide suspended in water containing a very small proportion of acetic acid.

The hiding power of a titanium dioxide pigment extended with chemically precipitated alkaline earth metal or zinc silicate was improved by reaction with carbon dioxide to convert the silicate to the corresponding carbonate. [66] A calcium carbonate pigment, free from particles larger than 6 microns and having an oil absorption of 20 or less, was produced by subjecting a mixture of crushed calcite and calcined titanium dioxide to continuous wet grinding at a slurry concentration of 450 g. to 550 g. solids per liter, diluting the mill effluent to 225 g.p.l. to 275 g.p.l. solids and classifying centrifugally to separate the fines. [67] The coarse material was returned for further grinding.

The color, tinting strength, and other pigment properties of lithopone may be improved appreciably by the addition of titanium dioxide. For greater effectiveness and economy, finished titanium dioxide pigment is often blended with regular grade lithopone, either as pastes or slurries in water, after which the composite product is dried and pulverized. Satisfactory results may also be obtained by

mixing the components in the dry state, but by this procedure it is difficult to get a uniform composition having the maximum pigment properties. On the other hand, if hydrous titanic oxide is precipitated on or mixed with the lithopone, subsequent calcination to a degree sufficient to develop the optimum pigment characteristics of the titanium dioxide may decompose the zinc sulfide and otherwise injure the lithopone component. Commercial pigments of this type normally contain approximately 15 per cent titanium dioxide.

O'Brien [68] produced satisfactory blends of 5 to 20 parts titanium dioxide with 80 to 95 parts, by weight, of lithopone in both wet and dry conditions. According to the former procedure, titanium dioxide of pigment grade was suspended in water and added to and thoroughly mixed with the desired amount of lithopone, also in aqueous suspension. The resulting mixture was filter-pressed, dried, and ground to a powder. In the second, the finely divided dry pigments were thoroughly stirred in a suitable mixing apparatus to get a uniform composition. By a coprecipitation process, [69] titanium dioxide was suspended in zinc sulfate solution and an equivalent amount of barium sulfide solution was introduced to precipitate barium sulfate and zinc sulfide which carried down the titanium dioxide particles. The system was then thoroughly mixed, after which the composite product was filter-pressed, muffled, quenched in water, ground wet, again filter-pressed, dried, and ground. As before, the proportion of titanium dioxide in the finished pigment ranged from 5 to 20 per cent.

Composites of this type have also been produced by precipitating all the components together. [70] A solution of titanic sulfate was treated with zinc carbonate or oxide, and after boiling the titanic acid was filtered off. More of the zinc compound was added to the filtrate, and it was freed from iron and other heavy metals by conventional methods. This purified zinc sulfate solution was mixed with the titanic acid obtained in the first step and an equivalent amount of barium sulfide was added. The composite precipitate was filtered, washed, and heated to incandescence to obtain a pigment containing titanium dioxide, barium sulfate, and zinc sulfide (lithopone).

Ireland and Mills [71] deposited a coating of not more than 2 per cent titanium dioxide on the particles of zinc sulfide and barium sulfate before calcination. In carrying out the process, the required amount of titanic sulfate solution was mixed with aqueous zinc sulfate and acetic acid and an equivalent amount of barium sulfide liquor was added to effect precipitation. The acetic acid held the titanium in solution during this stage of the operation, but it was later neu-

tralized with alkali to precipitate hydrous titanium oxide on the suspended particles produced in the previous step. The product was washed and calcined to give a three-component pigment.

Jaeger [72] heated the hydrolysis product of ilmenite solution with strong sulfuric acid in the presence of zinc sulfate, and the reaction product was ground, mixed with sodium chloride, and heated at 300° to 700° C. to effect decomposition of the sulfates. The sintered mass was washed with water to remove salts, leaving a residue of titanium dioxide and zinc oxide. On calcination, this product gave a pigment having good color and hiding power. Composite pigments having a zinc sulfide base were prepared by Thompson and Gardner.[73] Hydrous or calcined titanic oxide was suspended in a solution of zinc sulfate and an alkali metal sulfide was added to precipitate the zinc compound as sulfide on the suspended particles. Three-component pigments were prepared in a similar manner by employing a composite base such as that obtained by hydrolyzing titanium sulfate solutions in the presence of extenders (barium sulfate, calcium sulfate). In any case, the mixed precipitate was washed, calcined, and pulverized. By a similar procedure titanium dioxide was suspended in a solution of zinc sulfate, and sodium carbonate was added to precipitate the zinc carbonate.[74] As an example, 194 pounds of titanium dioxide was mixed into 1000 pounds of zinc sulfate solution containing 10 per cent zinc, and 658 pounds of sodium carbonate as a thin slurry was added, with vigorous stirring. The mixed precipitate was filtered, washed, dried, and ground to give a pigment containing 20 per cent titanium dioxide and 80 per cent zinc carbonate.

The relatively pure titanium dioxide and alkaline earth sulfate base composites have been blended mechanically with other pigments, such as zinc oxide, white lead, basic lead chromate, minium, basic lead sulfate, calcium carbonate, and mineral fillers, to obtain products having specific properties.[75] A three-component pigment was formed by carefully blending 35 to 50 parts, by weight, basic lead carbonate, 18 to 35 parts zinc oxide, and 35 to 50 parts titanium dioxide.[76]

Chapter 14

CALCINING, MILLING, AND PROCESSING TITANIUM DIOXIDE TO PRODUCE PIGMENTS

Treatment and Calcination of Hydrous Titanium Oxide

The thoroughly purified and washed precipitate obtained by the thermal hydrolysis of titanium salt solutions is the amorphous hydrous oxide which contains some closely held acid. In the production of pigments, a calcination step is necessary to drive off the water and residual acid and at the same time convert the titanium dioxide to crystalline form. This is accompanied by an increase in the index of refraction, and consequently opacity, and at the same time desired pigmentary properties are developed.

In 1844 Rose [1] obtained amorphous titanium dioxide as a white powder, and noted that its specific gravity varied according to the temperature to which the material had been subjected. For example, a sample calcined at 600° C. had a density of 3.92, and another heated to 1000° and 1200° C. was further increased to 4.25. According to Heaton [2], calcination converted titanium oxide from the amorphous form having an index of refraction of 1.8 to the anatase crystal form having an index of refraction of 2.55 and finally to the rutile modification with a further increase in refractive index to 2.71. A mixture of titanium dioxide with barium sulfate and calcium sulfate, similarly ignited, exhibited an effective index of refraction far above the mean value of the two constituents. This was attributed to a coating of highly refractive titanium dioxide on the individual particles of the alkaline earth metal sulfate and to an intercrystallized mixture of the two materials to produce additional reflecting surfaces within the larger particles of the extender.

Amorphous titanic oxide or hydroxide, such as is obtained from sulfate solution, was converted to the cryptocrystalline modification [3] of pigment grade by calcination at 900° to 1000° C. The end point was determined by microscopic examination. Conversion was accelerated by the addition of 5 per cent zinc chloride or ammonium

fluoride. During the change to cryptocrystalline form, the index of refraction was raised from 2.2 of the amorphous material to 2.55 for anatase, 2.64 for brookite, and 2.71 for rutile, with corresponding increases in tinting strength. Sulfuric acid, water, and other volatile materials were driven off. No change in particle size took place on conversion to crystalline form. Mixtures of titanic oxide

Figure 8. Rotary pigment calciners, showing the burners

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and such fillers as barium sulfate and calcium sulfate, after calcination, consisted of a cryptocrystalline mass of the titanium dioxide embedded in a matrix of the extender.

In the commercial production of titanium dioxide pigments, calcination is necessary in order to develop maximum opacity and covering power. In general, these properties are dependent upon the coincidental increase in refractive index of the particles. At the higher range of temperature, development of these properties is accompanied by a partial or complete change in crystal structure from anatase to rutile. This conversion takes place more rapidly above 900° C., but at this temperature there is a danger of producing a

somewhat discolored product. Below this value the last traces of sulfuric acid are expelled with difficulty. However, if the hydrous titanium oxide is treated with a small proportion of an accelerator the desired transformation can be accomplished at 850° to 900° C. in a shorter time, thus helping to avoid discoloration.[4] Compounds which functioned as accelerators were the hydrates, sulfates, nitrates, and carbonates of potassium and sodium, and sulfates of aluminum and magnesium. Proportions of 0.5 per cent were usually sufficient. These agents not only hastened crystallization but also greatly improved tinting strength and covering power of the resulting products. Pigments processed in this manner had lower oil absorption, and their reaction, as measured by pH, was nearly or quite neutral, depending upon the degree of calcination and the nature and amount of the addition agent. If the accelerator was used in such a proportion, for example 0.75 per cent, that some of it remained soluble in water, the calcined material was washed and dried before grinding, or this was accomplished incidental to wet milling.

Pigments prepared in this manner were characterized by clear white color, excellent brightness, covering power, and resistance to discoloration in light. These relationships are presented quantitatively in the table below. All samples were calcined for the same period of time at 875° C.

TABLE 8

EFFECT OF POTASSIUM SULFATE ADDITIONS ON THE PROPERTIES
OF THE FINAL PIGMENT

Property	Addition Agent		
	None	0.5% K_2SO_4	0.75% K_2SO_4
Reaction	Very acid	Slightly acid	Very slightly acid
Crystal structure	Octahedrite with much rutile	Octahedrite with considerable rutile	Octahedrite with some rutile
Hiding power (sq. cm. per gram)	105	124	147
Oil absorption (parts oil per 100 parts pigment)	36	32	31
Water insoluble salts (calculated as per cent Na_2SO_4)	0	0.24	0.45

Pigments of superior whiteness and opacity were obtained by treating washed titanic oxide pulp with 0.5 to 6.0 per cent of an

alkali metal compound [5] before calcination. Such products were neutral or slightly alkaline in reaction, as determined by pH measurements. The added agents, which assisted the sintering action, were removed from the pigment by subsequent washing or by wet milling. This treatment was also applicable to mixtures of titanium dioxide and such extenders as barium sulfate and calcium sulfate. In an actual operation, 30 parts by weight of a pulp obtained by hydrolytic precipitation from ilmenite solutions, and containing 10 parts of titanium dioxide, was intimately mixed with 0.05 part potassium carbonate and heated at 800° to 1000° C. for 2 hours. The original pulp contained sufficient residual sulfuric acid to convert the carbonate or hydroxide conditioning agents to sulfates. After calcination the product was washed to remove the potassium compounds. However, if the pigment was later ground by the wet process, all soluble compounds were extracted as an incidental phase of this operation. The improvement in color of the finished pigment was found to be a function of the alkali metal and was independent of the acid radical associated with it.

A pigment of improved brightness and tinting strength was produced by adding 0.5 to 2.5 per cent of an alkaline earth metal chloride to the hydrous titanium oxide before calcination.[6] Monk [7] added an oxide of aluminum, gallium, indium, silicon, germanium, or tin, together with an oxide of beryllium, magnesium, calcium, strontium, barium, or zinc, to hydrolytically precipitated titanium dioxide before calcination to neutralize colored impurities and yield a pigment of improved color and brightness.

Rhodes [8] calcined hydrous titanium oxide in a similar manner with 1 to 2.5 per cent of an alkali or alkaline earth metal titanate to produce a pigment of greater opacity, better miscibility, and lower oil absorption.

Uncorrected pigments have a characteristic yellow tone which is undesirable for many purposes. This discoloration may be intensified by a number of factors, such as the nature of the ore used, the conditions of manufacture, and impurities picked up during processing. The intensity of the yellowish cast generally increases to a maximum on exposure to actinic light. Although this undesirable coloration may be neutralized by blending with a pigment of similar composition having a bluish tone, the brightness or total reflectance of the product would be lowered.

White pigments having a neutral or bluish cast may be obtained without sacrificing brightness and without adversely affecting other

essential properties by mixing with the hydrous oxide, before calcination, 0.001 to 0.04 per cent, based on titanium dioxide content, of one or more of the elements tungsten, molybdenum, erbium, lanthanum, tin, palladium, platinum, and thorium as convenient salts.[9] Products obtained in accordance with this procedure had a high stability to light, that is, they did not discolor on exposure to actinic rays. Working with ilmenite of the Norwegian type which had a strong tendency to give titanium dioxide possessing a relatively high degree of discoloration, a higher proportion of the conditioning agent was required.

For example, a solution of sodium tungstate containing 80 g. of tungsten was added to a washed paste of 1000 kg. titanium dioxide. After thorough mixing, the product was dried, calcined at 850° to 1000° C., and pulverized, to yield a final pigment having a gray-blue tone. Other essential pigmentary properties were not influenced appreciably by the treatment.

In a similar manner, pigments with a neutral white or slightly bluish cast were obtained by calcining hydrous titanic oxide in the presence of a very small quantity of a compound of tungsten or molybdenum, and subjecting the product, during or after the calcination step, to the action of a reducing gas such as hydrogen or carbon monoxide at an elevated temperature for a short period of time.[10] The effect was also produced by adding a small amount of a carbonaceous material that liberated a reducing gas on ignition. A desirable bluish tone was developed by exposing a pigment containing 0.001 per cent tungsten to the action of hydrogen at 900° C. for one fifth second.

According to Heaton,[11] the yellowish color which often develops during the calcination step is not due, as originally thought, to the presence of impurities, but rather to the formation of rutile. This conversion does not take place if a small proportion of the titanium is present as a phosphate compound. A pigment of improved quality was obtained on refining crude titanium dioxide by a process involving calcination with phosphoric acid.[12] In an example, a pulp of hydrous oxide containing small amounts of iron compounds and sulfur trioxide was agitated with a mixture of sulfuric and phosphoric acids so that the final mix contained 2.5 per cent phosphorus pentoxide. After preliminary reaction the mass was ground with 1.4 parts sodium chloride for each part of titanic oxide, and the mixture was heated to 300° to 700° C. Free hydrochloric acid was given off. The ignited mass was cooled, crushed, and lixiviated, and the

residue was dried and ground to obtain a white or light-colored pigment containing combined phosphorus.

Washburn [13] produced a soft white pigment by calcining hydrous titanic oxide or a composite mixture with calcium sulfate or barium sulfate in the presence of a small proportion of phosphoric acid or calcium phosphate at a temperature below the fusing point. The wet pulp was mixed with phosphoric acid in the proportion of about 15 parts phosphorus pentoxide to 100 parts titanium dioxide and calcined at 950° C. for 2 hours to drive off the water and effect crystallization. Alternatively, the hydrous oxide was first dried, the phosphoric acid was added, and the mixture was calcined as before.

Titanic oxide formed by the thermal hydrolysis of sulfate solutions carries down with it most of the phosphate present so that instead of adding phosphoric acid to the pulp in a separate step it may be added in the proper proportion to the ilmenite solution before precipitation.[14] The phosphate acquired in this manner is not removed by washing with water. Phosphoric acid, phosphates, chlorides, fluorides, and organic compounds may be added to coalesced barium sulfate composite pulp before calcination as sintering agents to improve the color and other properties of the resulting pigment.[15] Alkali metal compounds and neutralizing agents may also be incorporated, in accordance with conventional practice. The color, brilliance, and covering power of alkaline earth sulfate composites were improved by the incorporation of boric acid or a borate,[16] as of calcium or barium, before calcination. Hydrous titanium oxide, as obtained by the thermal hydrolysis of ilmenite solutions, was freed from residual sulfuric acid by neutralization followed by washing. For the successful operation of the process it was necessary that the pulp be slightly alkaline rather than acid. Boric acid or a borate (calcium borate) in the proportion of 2 to 4 parts by weight to 100 parts titanium dioxide was added and the constituents were thoroughly mixed. The suspension was dewatered and ignited at 700° to 900° C., depending upon the time of exposure to develop pigmentary properties.

Allan [17] calcined titanium oxide or titanates with a small proportion of a compound of fluorine (fluotitanic acid, sodium fluoride, magnesium fluorotitanate, or hydrofluoric acid), which does not volatilize immediately at the temperature employed. Hydrofluoric acid reacted fairly rapidly to form a titanium fluoride compound in which the fluorine was fixed. In an example 1 g. hydrofluoric acid as a 60 per cent solution was added to 100 g. titanium dioxide of the hydrous form as a slurry. The mixture was stirred thoroughly,

dewatered, and calcined at 850° C. for 2 hours to produce an extremely soft white pigment having good covering power and a slightly acid reaction.

Improved properties were obtained by carrying out the calcination in an atmosphere containing vapors of zinc, antimony, cadmium, aluminum, or lead or their compounds.[18] These metallic agents were effectively introduced into the furnace atmosphere as suspensions in the fuel oil. Similar results were obtained by heating hydrous titanium oxide at 800° to 1000° C. with metallic aluminum, chromium, iron, vanadium, or rhenium, or with the corresponding oxide and a trivalent titanium compound.[19] According to another modification, hydrous titanium oxide in a finely divided state of subdivision was heated at 800° to 1000° C. to effect crystallization and develop pigmentary properties.[20] This operation was conveniently carried out by spraying the material directly into a furnace maintained at the proper temperature. Residual sulfuric acid was removed from the pulp by neutralization, followed by washing before the calcination step. The method proved to be equally applicable to composite products, particularly those containing alkaline earth metal sulfate extenders.

To eliminate the necessity of regular calcination, an aqueous suspension of purified titanic acid obtained by the hydrolysis of a dilute solution was autoclaved at 375° to 500° C. and the corresponding pressure.[21]

By heating hydrous titanium oxide (precipitated by the thermal hydrolysis of sulfate or chloride solutions) under pressure with water near the critical temperature, in the presence of 0.01 to 0.02 equivalent of hydrochloric or sulfuric acid or an acid salt, the desired pigment properties were developed and the usual high temperature calcination step was not necessary.[22] Autoclave pressures corresponding to the vapor pressure of the solution at 250° to 375° C., or even higher, were employed. Composite pigments containing barium sulfate, calcium sulfate, and zinc oxide may also be processed according to this method.

Ancrum and Oppegaard[23] obtained pigments having a high brightness, a neutral to bluish tone, and an exceptional fastness to light by calcining the hydrous oxide with not more than 0.1 per cent antimony as a convenient compound. Although the commercial trioxide proved quite satisfactory and economical, any compound of antimony may be used. This treatment was also effective in the presence of extenders and other conditioning agents such as alkali metal salts, phosphoric acid, fluoride compounds, and borates.

Furthermore, antimony compounds allowed more latitude during calcination; that is, higher temperatures could be employed without injurious effects. A washed hydrolysis product calcined with 0.01 to 0.03 per cent antimony trioxide, based on titanium dioxide, gave pigments with a neutral white to bluish cast, possessing particularly good brightness, fastness to light, and tinting strength.

Similar improvements in tinting strength and color were obtained by incorporating a small proportion of a compound of a rare earth element having atomic number between 59 and 71, or of cerium, lanthanum, or yttrium,[24] with the hydrolytically precipitated pulp before calcination. Proportions of 0.02 to 0.50 per cent gave optimum results. Phosphoric acid or phosphates in the ratio of 0.10 to 2 per cent, expressed as phosphorus pentoxide and based on the titanium dioxide, were also added to the hydrolysis solution. In a particular case, 0.10 g. cerium sulfate was added to 1 liter of a solution containing the equivalent of 15 per cent titanium dioxide, 29 per cent sulfuric acid, and 14 per cent ferrous sulfate, and the resultant solution was subjected to thermal hydrolysis. Practically all the cerium and phosphate compounds came down with the titanium. The precipitate was filtered, washed, and calcined according to conventional practice.

Similarly, titanium dioxide pigments of good brightness, tone, fastness to light, and softness were produced by calcining hydrous titanium oxide obtained by the thermal decomposition of ilmenite solution after incorporation of a small proportion of a compound of columbium or tantalum.[25] From 0.01 to 2 per cent of the conditioning agent was employed, and the addition could be made at any time prior to calcination. Such compounds or minerals were mixed with the ilmenite ore before reaction, or to the solution in the form of a soluble salt before precipitation, or to the washed hydrolysis product. Frequently, if the calcination was carried out without treatment to such a degree as to obtain maximum tinting strength and hiding power, these desirable properties were accompanied by a tendency of the pigment to acquire a grayish, yellowish, or reddish tone, and in some cases to exhibit a lack of fastness to light and an excessive hardness, thus rendering the product difficult and expensive to grind. From 0.01 to 0.10 per cent columbium effectively overcame these undesirable effects.

In an example, 1000 g. ilmenite was mixed with 510 ml. of 93 per cent sulfuric acid, 2 ml. of 85 per cent phosphoric acid, and 0.2 per cent columbite, based on the titanium dioxide content of the ore,

and the charge was added to 370 ml. of 93 per cent sulfuric acid, previously heated to 130° C. in a cast-iron pan. The mixture was heated, with stirring, to fumes of sulfur trioxide, and 40 ml. of water was added to initiate the reaction. After the reaction had gone to completion, the mass was baked for 30 minutes at 200° C., cooled, and leached with water at 60° C. The solution was adjusted to a specific gravity of 1.50 and reduced with scrap iron to a titanous oxide content of 3 g. per liter, after which it was clarified and cooled to 27° C. to remove part of the ferrous sulfate by crystallization. The mother liquor was concentrated by vacuum evaporation to a gravity of 1.60 and hydrolyzed in an autoclave by heating for 80 minutes at a temperature corresponding to a superpressure of 20 pounds. After thorough washing the pulp was treated with 0.6 per cent potassium carbonate, calcined at 970° C. for 3 hours, and finished by the usual methods.

Titanium dioxide treated with columbium in accordance with this procedure could be subjected to a more intense calcination to develop maximum tinting strength without adversely affecting the other properties. Furthermore, the temperature range for optimum calcination was considerably increased, and values up to 1100° C. could be employed.

Ryan and Cauwenberg [26] incorporated 2.5 to 10 per cent of a carbonaceous material such as sugar, dextrin, starch, or oil with hydrous titanium oxide and baked the mixture at 200° to 400° C. before calcination. For convenience and economy the two steps were carried out in the same furnace. The method proved applicable to composite pulps containing alkaline earth metal sulfates. In a specific operation, a precipitate obtained by the thermal hydrolysis of a sulfate solution of ilmenite was thoroughly washed and mixed with 5 per cent, based on the dry weight, of fuel oil. The composition was then dried and baked at 250° C. for 6 hours, and finally calcined at 750° to 900° C. Pigments processed in this manner were pure white and contained a minimum of impurities.

According to a related procedure, the washed pulp was treated with 2 to 20 per cent of a carbonaceous material such as charcoal, starch, sawdust, or oil, and then calcined at 750° to 900° C. [27] The carbonaceous material was burned off in the processing, leaving a pure white titanium dioxide containing a minimum of impurities and having excellent properties.

Pigments of very fine particle size [28] were said to be obtained by treating freshly precipitated titanium dioxide with gelatin, starch,

or dextrin to transform part of the product into the colloidal state before calcination. According to a similar procedure, the hydrous oxide was dispersed with a peptizing agent, such as hydrochloric acid, nitric acid, or barium chloride, and coagulated.[29] The treated pulp was then washed, dried, and calcined above 840° C. to obtain porous particles of titanium dioxide having a high opacity and soft texture. In incident light the pigment presented a certain number of plane faces inclined in various directions. By employing barium chloride as dispersing agent and barium carbonate as coagulating agent, the corresponding titanate was produced.

Crystalline titanium dioxide was produced by heating the hydrous material previously dried at 110° C. in a compound of the same crystalline structure (magnesium sulfate) at a temperature below the melting point, 900° C.[30] By calcining a wet mixture of titanium dioxide and barium sulfate, Buckman[31] obtained a pigment in which these components were combined or heat compacted.

White titanium dioxide pigments having a controlled subordinate tint [32] were obtained by heating the regular calcined product to 900° to 1000° C. and cooling in air to 750° C. under carefully regulated conditions. If such cooling took place, in a few seconds a pronounced blue cast developed, while if the temperature was gradually reduced, in 5 minutes or longer a decided yellow tone resulted. By bringing about the cooling at rates between these limits, any desired tone from distinct blue to distinct yellow was obtained. Commercially, the titanium dioxide was discharged from the calciner at about 900° to 1000° C., and controlled cooling was effected easily and economically at this stage.

According to Parravano and Caglioti,[33] the pigmentary properties of titanium dioxide depend upon the sulfuric acid content of the hydrolysis product and the nature and amount of mineralizers added, and particularly upon the temperature and time of calcination. Such products crystallized at about 500° C. as anatase, and although some samples were transformed into rutile by calcination at 825° C., others showed the spectrum of anatase even after calcination at 950° C. for 1.5 hours. The velocity of the process of crystallization was dependent at all temperatures on the sulfur trioxide content of the hydrolysis product. Conditions which resulted in the formation of rutile did not in general produce good pigment properties. The temperature of drying the hydrous oxide before calcination was reported to have no influence on the properties of the finished pigment.[34]

Hydrous titanium oxide of the anatase modification is generally treated with a potassium compound before calcination to obtain higher tinting strength and improved color, and the rutile product may be improved by such treatment, particularly if the upper temperature range is employed. Other conditioning agents may also be included along with the alkali metal compound to bring out special and specific properties. Alkaline earth metal sulfate base composites are quite resistant to sintering, and the potassium treatment is in general not essential.

According to a commercial method,[35] the washed and treated titanium dioxide cake is fed directly from the continuous filters to a rotary, oil-fired furnace where it is completely dried and finally brought to a temperature of 1000° C. at the discharge end. Calcination is one of the most critical steps in the manufacturing process. Too high a temperature or too long an exposure to a lower temperature may cause the product to become gritty and may injure the color, while undercalcination, although generally productive of good color, does not bring out the maximum tinting strength and covering power. Passage through the kiln requires considerable time—in the neighborhood of 24 hours—and control of both temperature and atmosphere at every point along the course is important.

Rutile from Sulfate Solutions

The hydrolytic decomposition of titanium sulfate solutions by the more common methods, as by boiling direct, by mixing hot with hot water, by heating at atmospheric pressure in the presence of seeding materials prepared from sulfate solutions, and by heating in an autoclave, yields titanium dioxide of the anatase crystal modification. These methods have been treated in detail in previous sections.

By seeding regular sulfate solutions with rutile nuclei, however, the entire titanium dioxide content may be precipitated hydrolytically in a condition possessing the rutile crystal form.[36] For example, an alkali metal titanate was first formed by heating a mixture of 100 pounds pure titanium dioxide and 100 pounds sodium hydroxide free from sulfates at 700° C. for 1 hour. It was then cooled and lixiviated with 10 per cent hydrochloric acid until neutral to methyl orange, and the product was added to 500 gallons regular sulfate solution containing 250 g. titanium dioxide, 25 g. ferrous iron, and 575 g. sulfuric acid per liter, and the seeded charge was boiled for 4 to 5 hours to effect hydrolysis. Titanium dioxide precipitated in this manner had the rutile crystal form, and

on calcination gave a pigment having one third higher tinting strength than the usual anatase product.

Any of the alkali hydroxides or any of the halogen acids may be used in the process, and the seeding crystals, once formed, will function efficiently in the sulfate solution, yielding an artificial rutile type titanium dioxide having the same crystal form as the natural material.

By hydrolyzing sulfate solutions previously seeded with a nucleating sol prepared by heat-treating a dilute solution of the tetrachloride, titanium dioxide of pigment grade was obtained, which on calcination at moderate temperatures (around 900° C.) had the rutile crystal form and the correspondingly high tinting strength.[37] Pure solutions of the tetrachloride gave a product of better opacity and other pigment properties, although the presence of iron and organic impurities was not detrimental to effective nucleating properties of the heat treated sol. As in other methods, any iron salts were reduced to the ferrous state. Heat treatment of the sol developed the nucleating power to the maximum degree, and both temperature and time were regulated, since overcuring reduced the effectiveness of the product. It follows that longer periods of heating were required at lower temperatures than at higher temperatures. Best results were obtained by heating a tetrachloride solution containing the equivalent of 10 g. to 20 g. titanium dioxide at 80° to 85° C. for 10 to 15 minutes. The cured sol presented a slight opalescence, and the particles could not be separated by the conventional methods of filtration and washing. Degree of dispersion of the colloidal titanium oxide and its homogeneity did not seem to have a great influence on the nucleating properties, and mixtures of products having various degrees of dispersion were used as seed with satisfactory results. The method is generally applicable to solutions of all titanium salts such as sulfate, chloride, and nitrate from which the oxide may be precipitated by thermal hydrolysis, but the latter two would normally yield rutile.

Although ilmenite solutions of wide limits of concentration may be successfully hydrolyzed with such seed, better results were obtained by employing basic solutions containing 130 g. to 150 g. per liter titanium dioxide and sulfuric acid free and combined with titanium less than that corresponding to the normal salt. The proportion of nuclei was from 9 to 12 per cent of the total titanium component; in general, the greater the basicity of the solution, and the higher the concentration of titanium, the smaller the proportion of nuclei required.

With chloride and nitrate solutions the concentration was from 140 g. to 160 g. titanium dioxide equivalent per liter, and the proportion of nuclei was from 5 to 9 per cent.

Employing a sulfate solution containing 140 g. to 150 g. titanium dioxide per liter and having a basicity corresponding to a proportion of titanium dioxide to active acid of 1.0 to 1.4, about 10 per cent nuclei gave the best results. If the concentration of titanium dioxide was raised to 200 g. per liter or more, by maintaining this degree of basicity the quantity of nuclei could be reduced. On the other hand, if the basicity was increased to a proportion of titanium dioxide to active sulfuric acid of 1.0 to 0.84, and the concentration of titanium dioxide held at 140 g. per liter, 7.5 per cent nuclei gave best results.

The method of mixing exerted a certain influence on the results obtained and it was found advantageous to add the solution to the nucleating sol. Carrying out the hydrolysis at the normal boiling point, 97 per cent recovery was obtained in 15 minutes to 1 hour. More rapid hydrolysis was effected at temperatures corresponding to superatmospheric pressure. The method was also applicable to continuous operation.

For example, one liter of titanium tetrachloride solution containing the equivalent of 10 g. titanium dioxide was heated under reflux, with stirring, to 85° C. and held at this temperature for 12 minutes to develop the nucleating property. At 65° C. the opalescence began to develop. After 12 minutes at 85° C., heating was discontinued and 700 ml. of a sulfate solution containing 150 g. titanium dioxide, 265 g. active sulfuric acid, 170 g. ferrous sulfate, and trivalent titanium equivalent to 1.2 g. per liter of the dioxide was added. During the addition the temperature dropped to 60° C. and the system was then heated to boiling in 20 minutes. Hydrolysis was complete after boiling for 15 minutes, and a recovery of 96 per cent was obtained. The product was cooled to 80° C. and the precipitate was filtered, washed, dried, calcined, and pulverized according to the conventional methods to produce a white pigment of the rutile crystal modification. It had uniform particles of 0.5 to 0.6 micron and was practically free of aggregates and of particles greater than 2 microns. Tinting strength by the Reynolds method was 1625.

Barksdale and Plechner [38] prepared nuclear suspensions of the rutile type by heat-treating dilute titanic chloride solutions to which an alkaline agent such as calcium oxide, sodium hydroxide, and potassium carbonate had been added in an amount equivalent to from one fourth to one half of the potential hydrochloric acid.

Acid-poor solutions obtained in this manner were diluted to the equivalent of 10 g. to 30 g. titanium dioxide per liter, and heated at 85° to 95° C. for approximately 10 minutes to develop the nucleating properties to the maximum degree. The proper cure was characterized by the development of an opalescent appearance and was a function of both temperature and time of heating. Sulfate solution of ilmenite at 80° C. was added slowly, with constant agitation, in such proportions that the titanium dioxide furnished by the nuclei was from 4 to 10 per cent of the total. The seeded mixture was heated to boiling and refluxed until the recovery exceeded 90 per cent; this in general required only ½ hour. The hydrolysis product was filtered, washed, calcined, and milled in the usual manner to produce a pigment characterized by titanium dioxide of the rutile crystal modification and the correspondingly high tinting strength.

In a specific operation, a portion of a titanium tetrachloride solution containing the equivalent of 15 g. titanium dioxide and 25 g. hydrochloric acid was treated with 7 g. of hydrated lime, diluted to 1 liter, heated to 85° C., and held at this temperature for 10 minutes to develop the nucleating properties. To this nuclear suspension was added in 15 minutes 1000 ml. of a sulfate solution of ilmenite containing 250 g. titanium dioxide, 495 g. active sulfuric acid, and 190 g. ferrous sulfate at 95° C.; the seeded mixture was heated to boiling in 20 minutes and refluxed for 1 hour. The hydrolysis product was filtered, washed, and calcined to produce a pigment of the rutile crystal form having high tinting strength.

Similar results were obtained by employing a nucleating composition prepared by heating a titanium tetrachloride solution containing the equivalent of 5 g. to 30 g. of the dioxide per liter, and 0.5 to 2.0 mole proportions of a nonoxidizing univalent anion such as chloride, metaborate, acetate, or formate at 80° to 90° C. for 10 to 15 minutes to develop a characteristic opalescence.[39] Approximately 5 per cent of this suspension accelerated and directed the hydrolysis of concentrated sulfate solution of ilmenite to produce pigment of the rutile crystal modification possessing the correspondingly higher tinting strength and brightness. McCord and Saunders[40] precipitated titanic acid which converted directly to rutile on calcination below 1000° C. by hydrolysis of sulfate solutions of ilmenite in the presence of gamma titanic acid as a nucleating agent.

By another approach, sulfate solutions nucleated or seeded with peptized oxides or hydroxides of titanium gave, on hydrolysis, a

precipitate which after calcination in the usual manner consisted of particles of the rutile structure of the optimum size for pigments, with a very high tinting strength and covering power.[41]   Such seeds were prepared by peptizing with a strong monobasic mineral acid, with the aid of heat, titanium oxide or hydroxide separately precipitated from a solution of a titanium salt by adding an alkaline reagent until the acidity of the solution was reduced to a value corresponding to a pH of 3 to 6. Peptization was disturbed by the presence of sulfates, and these were removed from the precipitated oxide or hydroxide by washing. In this process oxides or hydroxides of metals other than titanium, belonging to Group IV of the Periodic Table, prove effective.

Alternatively, before use in the hydrolysis the peptized seed was coagulated, for example by addition of alkali, and after being washed free from electrolytes was added in the form of a sol or gel to the sulfate solution to be hydrolyzed. The presence of phosphoric acid or a soluble phosphate during the precipitation of the seed and the later hydrolysis step was advantageous.

For producing the nuclei, a part of the sulfate solution to be hydrolyzed was removed and adjusted to an acidity not far from the neutral point by adding an alkaline agent. It was important that the neutralization be carried to a point corresponding to a pH of 3 to 6. This precipitate was washed until free from sulfates, and then peptized and converted into a sol by warming with a solution of a strong monobasic acid (hydrochloric) to develop the nucleating property. The composition was then added to the main part of the titanium sulfate liquor, after which the hydrolysis and calcination were carried out in the usual manner. Such seed proved to be extremely stable. In an actual operation, a solution was employed which was obtained by dissolving the reaction product of ilmenite with strong sulfuric acid and 1 per cent admixed phosphoric acid, and containing 200 g. titanium dioxide and 470 g. free sulfuric acid per liter. Thirty-two liters of this liquor was run into 120 liters of 9 per cent aqueous sodium hydroxide until a pH of 3 to 6 was obtained. The precipitate was filtered and washed free of sulfates, stirred into 38 liters of 10 per cent hydrochloric acid, and heated at 90° C. until the clear solution which first formed became opalescent. This colloidal solution was added to 1000 liters of the original ilmenite liquor and the mixture was boiled for 2 hours to effect hydrolysis. A yield of 95 per cent was obtained. The precipitate was filtered, washed, calcined, and milled in the same manner as anatase titanium dioxide.

A similar nucleating composition was prepared by peptizing in hydrochloric acid the hydrous titanic oxide precipitated from sulfate solution containing 1 per cent phosphoric acid by adding sodium hydroxide solution.[42] The nuclei were used with sulfate solutions of ilmenite to yield titanium dioxide of the rutile type on hydrolysis.

Bennett[43] obtained rutile by hydrolyzing titanium sulfate solution in the presence of a nucleating agent prepared by peptizing hydrous titanic oxide hydrolytically precipitated from sulfate solution at 45° to 70° C., after adding sodium hydroxide to adjust the acidity of the solution to a pH of 2 to 7. The peptized suspension, which contained 10 to 15 g.p.l. titanium dioxide, was added to the main solution in a proportion of 8.5 per cent based on the titanium dioxide content. The titanium content of the hydrolysis solution, after neutralization, was 55 to 75 g.p.l.

Similar results were obtained by employing titanium oxychloride as nucleating agent.[44]

Weber and Bennett[45] employed nuclei prepared by dispersing or peptizing in dilute nitric acid the thoroughly washed and neutralized precipitate obtained on hydrolysis of a dilute feebly acid solution of titanium sulfate. The final suspension had a pH less than 2 and possessed the properties of a colloidal solution. As an illustration of the operation of the process, a crystalloidal solution of specific gravity 1.07 containing 13 g. titanium dioxide, 4.5 g. iron as ferrous sulfate, and 31 g. sulfur trioxide per liter was boiled to effect thermal hydrolysis. A quantity of the washed paste corresponding to 5 pounds dry titanium dioxide was neutralized with sodium hydroxide. The soluble salt formed was washed out with water and the purified product was dispersed in 20 pounds of water containing 0.85 pound nitric acid (specific gravity 1.42) to the degree that practically all passed through a filter paper but all the solid component was retained on a colloidal membrane. The pH value was below 2. This suspension was diluted to a specific gravity of 1.1 and added to 1350 pounds of an ilmenite solution of specific gravity 1.35 containing 80 g. titanium dioxide, 30 g. iron (all in the ferrous condition), and 172 g. sulfur trioxide per liter. After thorough mixing the charge was heated to boiling and boiled for 3 hours to precipitate the titanium content as hydrous oxide. In this system 95 per cent of the titanium dioxide was contributed by the hydrolysis solution and 5 per cent by the nucleating suspension. The precipitate settled rapidly and on processing gave a pigment of improved color and tinting strength. Besides nitric acid, other monobasic acids, such as acetic and propionic, were effective.

A nucleating composition was prepared by adding an alkaline agent to a chloride solution to precipitate the titanium as hydrous oxide, and acidifying the suspension with hydrochloric acid.[46] A similar composition is prepared from the $H_4TiO_4 \cdot SO_3$ obtained as a precipitate by heating a water solution of titanyl sulfate.[47] The hydrated precipitate is treated with hot sodium hydroxide to remove excess acid and form sodium titanate which is washed with water and treated with hydrochloric acid to form a rutile seeding agent. From 1 to 5 per cent of the nucleating agent was added to titanyl sulfate solution to direct precipitation of titanium dioxide of the rutile crystal modification. Mayer[48] treated hydrous titanium dioxide, formed by heating the tetrachloride solution, with 4 to 55 millimole proportion of sulfuric acid as a stabilizer, and removed the chloride ions by dialysis. By another modification the hydrous titanium dioxide was peptized with a monobasic acid, heated with the stabilizing agent as before, and dialyzed to purify the nuclei.

A negatively charged colloidal solution of titanium dioxide, prepared by reversing the charge of the usual positive sol, was employed by Stark[49] to accelerate and direct the hydrolysis of sulfate or chloride solutions to produce pigment of the rutile form. Orthotitanic acid precipitated with ammonia from a tetrachloride solution was washed, added to 0.3 normal hydrochloric acid to get a concentration of 30 g.p.l. titanium dioxide, and peptized by heating at 80° C. for 20 minutes. The charge was changed to negative by adding 1.35 g. potassium citrate for each gram of titanium dioxide in the sol. After reversal of charge, the nuclei were added in a proportion of 3 to 5 per cent, based on the titanium dioxide content, to relatively concentrated sulfate or chloride solutions, and hydrolysis was effected rapidly by heating at 95° C.

The hydrous oxide obtained by incomplete hydrolysis of sulfate solutions gave rutile on calcination.[50] A nucleated concentrated titanium sulfate solution of low acidity factor, a mole ratio of H_2SO_4 to TiO_2 of 1 or less, was boiled to effect hydrolytic precipitation of 40 to 60 per cent of the titanium dioxide. The concentration of the solution did not fall below 40 g.p.l. titanium calculated as the dioxide. At this stage hydrolysis was interrupted and the product was filtered, washed, and calcined at 750° to 950° C. The finished pigment exhibited excellent rutile characteristics of high tinting strength and good color. Olson[51] employed a complex containing both anatase yield and rutile-inducing nuclei.

A suspension of colloidally dispersed (peptized) hydrous stannic oxide was found to induce the formation of rutile on hydrolysis of

titanium sulfate solution.[52] Precipitated stannic hydrate was washed thoroughly and peptized in a 0.05 to 1.0 normal solution of a monobasic acid, and the resulting dispersion was heated at 50° to 100° C. for a relatively short time to develop the nucleating properties to the maximum degree.

An indirect method for producing rutile pigments from anatase titanium dioxide as obtained by the regular hydrolysis of sulfate solutions involved conversion to barium titanate, solution in nitric acid, and reprecipitation of the hydrous oxide.[53] Keats [54] described a cyclic operation of the process in which the nitric acid and barium hydroxide were recovered and reused. Neutralized and washed hydrous oxide of the anatase modification, as obtained commercially by the thermal hydrolysis of sulfate solutions of ilmenite, was mixed with an equivalent amount of barium hydroxide and digested near the boiling point of the solution to obtain barium titanate. This compound was treated with 5 to 10 mole proportions of nitric acid of 30 to 50 per cent strength to form titanium nitrate and barium nitrate. Since barium nitrate is only slightly soluble in the strong liquor, the greater part of this constituent was present as crystals and these were separated readily by filtration or decantation. The solution consisting largely of titanium nitrate was adjusted to a concentration of 80 g. to 120 g. titanium dioxide per liter and hydrolyzed by boiling, after proper seeding, to produce a rutile precipitate. The hydrous material was filtered, washed, and calcined in the same manner as anatase hydrolyzates. In carrying out the hydrolysis, solutions of concentrations above 40 g. per liter titanium dioxide were employed; otherwise anatase was formed. The nitric acid filtrate from the hydrolysis product was collected for reuse, and the barium nitrate crystals were decomposed by heat to give oxides of nitrogen and barium oxide, both of which were reused.

In an actual operation, a washed iron-free pulp from hydrolysis of a sulfate solution of ilmenite was slurried in water and neutralized with ammonium hydroxide. All ammonium salts formed were washed out and the sulfate-free suspension was mixed with a chemically equivalent amount of barium hydroxide in aqueous solution. The slurry was heated to boiling and maintained for 1 hour to effect formation of barium titanate. This reaction product was dewatered and the cake was treated with cold 50 per cent nitric acid, with agitation. After several hours the mixture lost its opalescence and then consisted of crystals of barium nitrate in a titanium nitrate solution. Upon filtration about 80 per cent of the titanium was recovered before washing and the remainder by washing with cold

acidified, saturated barium nitrate solution. The main filtrate and washings were combined to give a solution having more than 80 g. titanium dioxide per liter, and this was subjected to thermal hydrolysis after addition of the proper seeding material. Precipitated hydrous oxide was filtered, washed, and calcined according to conventional methods to produce rutile titanium dioxide of pigment grade.

The barium nitrate crystals were decomposed by heat to give oxides of nitrogen which were recovered along with the nitric acid of the hydrolysis liquor for reuse. The residue of barium oxide was added to water to regenerate the hydroxide for attacking another batch of anatase pulp.

Similarly, orthotitanic acid precipitated from regular sulfuric acid solutions of ilmenite by adding an alkaline agent, such as ammonium hydroxide, was washed thoroughly to remove any divalent anions and dissolved in nitric acid, and the resulting solution was hydrolyzed to precipitate rutile titanium dioxide which was calcined to develop pigment properties.[55]

Rutile from Anatase

Hydrolytically precipitated titanium dioxide of the anatase crystal modification may be converted to the rutile form having desirable pigment properties by calcining at 850° to 1100° C. with a small proportion, generally 0.1 to 2.0 per cent, of zinc oxide or other compounds which will yield the oxide at the temperature employed;[56] with lithium chloride, titanate, or sulfate;[57] with inorganic compounds of magnesium, such as the metatitanates, which have the crystal characteristics of the spinel, corundum, ilmenite, phenacite, or sodium chloride crystallographic group;[58] or with antimony oxide[59] or a compound which will yield the oxide at the temperature employed.

Rutile of improved pigment properties was obtained by treating the anatase hydrolysis product with a small proportion of a mixture of zinc oxide and magnesium oxide,[60] or with a mixture of antimony trioxide with a compound of zinc, magnesium, calcium, or barium before calcination.[61]

Hydrolytically precipitated titanium dioxide which would normally yield anatase pigment was converted to rutile of improved pigment properties by direct calcination after mixing with a separately prepared compound of similar composition but which on calcination showed X-ray diffraction patterns of rutile.[62] Hydrous

oxide, as obtained from sulfate solutions, was seeded with 2 to 10 per cent of a similar product obtained from chloride solution before calcination to aid and direct conversion to the rutile form. Such a mixture, calcined at 900° to 1000° C. for 3 hours, showed 98 per cent rutile. By heating a mixture of 70 parts of the hydrolysis product of anatase with 30 parts of a hydrolyzate of the rutile form in an autoclave at superatmospheric pressure in a 50 g.p.l. hydrochloric acid solution, the entire product was converted to rutile of pigment grade without subsequent calcination.[63] The product was filtered, washed, and dried. Hydrolytically precipitated anatase was also converted to rutile by calcining first at 1000° to 1300° C. under reducing conditions, and then recalcining at 600° to 850° C. in an oxidizing atmosphere.[64]

Booge [65] calcined an anatase hydrolysis product precipitated from sulfate solutions by the Blumenfeld process (U.S. reissue 18,854), first at a temperature below 1000° C. in the presence of potassium sulfate or sodium sulfide to inhibit or prevent conversion to the rutile crystal form. The agent was removed by washing, and the product was recalcined at a higher temperature but below 1100° C. with approximately 1.0 per cent zinc oxide to effect conversion to the rutile crystal form. Rutile pigments of this type showed markedly improved resistance to chalking and fading. Peterson [66] found that by treating the hydrolytically precipitated anatase titanium dioxide with 0.5 to 0.75 per cent of a mixture of potassium sulfate and sodium sulfate and 0.25 per cent zinc sulfate, conversion to rutile could be effected by a single calcination at 975° C. Aluminum sulfate, magnesium sulfate, and barium sulfate could be substituted for the zinc sulfate.

Anatase titanium dioxide was also converted to the rutile crystal modification by a double calcination without accelerating agents.[67] Hydrous titanic oxide, as obtained from sulfate solutions, was first calcined in the usual manner with a negative catalyst (0.3 to 1.0 per cent of potassium sulfate) which retarded or inhibited rutile formation to develop pigmentary properties, and after reduction of the added agent by washing to less than 0.1 per cent, the pigment was recalcined to develop the rutile crystal structure.

From X-ray diffraction studies of titanium dioxide prepared and heated in different ways, Weiser, Milligan, and Cook [68] concluded that the rate of transformation of the more labile and less stable anatase modification into the less soluble and more stable rutile modification is opposed by two factors: retardation of the change by the adsorbed layer of ions on anatase which reduces its

rate of solution, and the acceleration of the change by the ionic environment in which anatase is more soluble. Anatase formed by hydrolysis of titanic chloride and titanic nitrate solutions changes fairly rapidly into rutile at 100° C. The rate of change is decreased enormously in the presence of a large excess of alkali chloride or nitrate because of the protective action of adsorbed ions, and is speeded up in the presence of an excess of hydrochloric or nitric acid, since the solvent action of the acid predominates over the protective action of adsorbed anions. Anatase formed by hydrolysis of titanic sulfate solution is not transformed into rutile in a reasonable time even in strong sulfuric acid solution, since strong adsorption of sulfate ions is a predominating stabilizing factor. Schlossberger [69] reported that the abnormal density-temperature curve of titanium dioxide indicated that sulfur trioxide was trapped in the anatase lattice and acted as a stabilizer in the transformation to rutile.

A rutile pigment was obtained by calcining washed precipitated titanium dioxide at 1000° C. with one sixth its weight of basic chloride $TiOCl_2$ and a small proportion of ferric ammonium sulfate. [70] Raw pigment anatase form of titanium dioxide is converted to the rutile modification by a disintegration treatment to reduce the particle size, followed by calcination at 750° to 1000° C. in the presence of 2 to 10 parts of added rutile and 0.5 to 1.0 per cent of an alkali metal salt to each 100 parts of anatase. The added rutile acts as a conversion promoter.

Neilsen and Goldschmidt [71] eliminated the residual acid by treating the washed pulp with calcium hydroxide or calcium carbonate to form insoluble sulfates, and then heated the mixture at 900° to 1050° C. to develop crystalline structure. By employing an excess of the calcium compound and prolonging the calcination, a pigment containing calcium titanate in cryptocrystalline form and an amorphous calcium sulfate was formed. A typical product contained 84.0 per cent crystalline titanium dioxide, 3.8 per cent calcium titanate, and 12.2 per cent calcium sulfate. Without an excess of the basic compound and without prolonged heating, titanium dioxide in the cryptocrystalline form was obtained. Alkaline earth metal carbonates as neutralization agents had the advantage of liberating carbon dioxide gas so as to render the product porous. [72]

Carteret and Devaux [73] obtained an acid-free product by treating the precipitated hydrous oxide with a solution of an alkaline earth metal chloride and then washing the reaction product with milk of lime or baryta to remove the hydrochloric acid. According to a

combination method,[74] a part of the closely held sulfuric acid was neutralized by treatment with an alkali metal hydroxide or carbonate, and the remainder with compounds such as oxides, carbonates, and chlorides of alkaline earth metals and lead (barium chloride), which yield insoluble sulfates. Residual acid was also removed by calcining the pulp in a constantly oxidizing atmosphere in the presence of calcium chloride, ammonium chloride, or other compound capable of forming insoluble or volatile sulfates.[75]

Dispersion, Hydroseparation, and Milling

In the manufacture of titanium dioxide pigments, the hydrolysis step tends to form a product of small particle size, but the subsequent calcination cements these into larger aggregates by compacting and sintering. To make the product suitable for most uses these aggregates must be broken down. Several methods of milling are applicable, depending upon the type of pigment and the purpose for which it is to be employed. The relatively pure oxide for incorporation into organic vehicles is generally submitted to a wet grinding and classification process. Such products for use in aqueous media, however, are normally ground in the dry state. Dry milling is in general more applicable to all grades of composite pigments, regardless of use.

Particles of 15-micron diameter are easily observed in paint films by the unaided eye, and under favorable conditions of lighting aggregates of 6 microns can be detected. These larger particles are particularly undesirable in the finished pigment, since they prevent the formation of a smooth, unbroken, and glossy paint surface. To a certain extent the aggregates can be broken down by the commonly employed grinding processes, such as passing through pebble or colloid mills, but these operations also act upon the smaller particles and reduce their size to an undesirable fineness. Screening cannot effect a separation of the coarser fraction to an appreciable extent, since the finest screen that can be used technically for this purpose, 325 mesh, has openings of approximately 40 microns.

Particles of 6 microns and larger contained in the calcined product can, however, readily be separated from the smaller fractions by an aqueous deflocculation process followed by elutriation.[76] The deflocculation must be closely controlled, and the alkalinity of the slurry should correspond to a pH between 7.2 and 10.0. If it is much above this range, the pigment will not be deflocculated to the

extent that a good separation by elutriation can be obtained. Ordinarily, aqueous suspensions of the calcined product do not show any material separation of large from small particles in an elutriation process. Sodium hydroxide, sodium carbonate, sodium silicate, trisodium phosphate, and ammonium hydroxide are the most effective and commonest dispersing agents. It is interesting to note that hydrochloric acid and similar compounds, which are so powerful for dispersing hydrous titanium dioxide, are entirely useless in connection with the calcined material. A dispersion of a 1 to 7 slurry suitable for use in the elutriation process should not show any settling on standing for 10 to 30 minutes or any flocculates in the suspension. Such a stability was obtained by adding 0.11 per cent sodium hydroxide, based on total solids content, to a neutral suspension of calcined titanic oxide until a pH of 9.6 resulted. The following table shows optimum amounts of various agents for producing dispersions of calcined pigment having the required stability.

TABLE 9

Optimum Amounts of Various Agents for Deflocculating Calcined
Titanium Dioxide Pigment

Deflocculating Agent	Per Cent Based on Weight of Pigment	Concentration of Slurry (approximately)	pH of Slurry
Sodium silicate	2.38	1-7.5	9.6
Sodium hydroxide	0.11	1-6.8	10.0
Ammonium hydroxide	9.50	1-8.7	9.6
Trisodium phosphate (dodecahydrate) .	0.71	1-6.9	9.2
Sodium carbonate	0.18	1-6.8	8.0

Larger or smaller amounts than those given in the table can be used effectively, provided that the pH of the suspension is kept within the workable limits of 7.2 to 10.0. Sodium hydroxide dispersed perfectly at 0.11 per cent, and half of this proportion yielded fair dispersions.

After deflocculation the suspension is caused to flow upward through an elutriation vessel at such a rate that the larger, heavier aggregates settle against the current of the liquid and fall to the bottom of the container, while the smaller particles are entrained and overflow with the liquid. A convenient type of elutriation apparatus for commercial application is the Dorr hydroseparator which in its essential parts consists of a cylindrical tank with revolving rake, central submerged feed, and overflow or launder.

Other forms of equipment such as the Callow cone or simple rectangular vats may be used.

The relationship between speed of upward flow of a well-deflocculated aqueous suspension of calcined titanium dioxide and size of the largest particles that are carried over by the overflow is shown graphically by the curve in Figure 9.
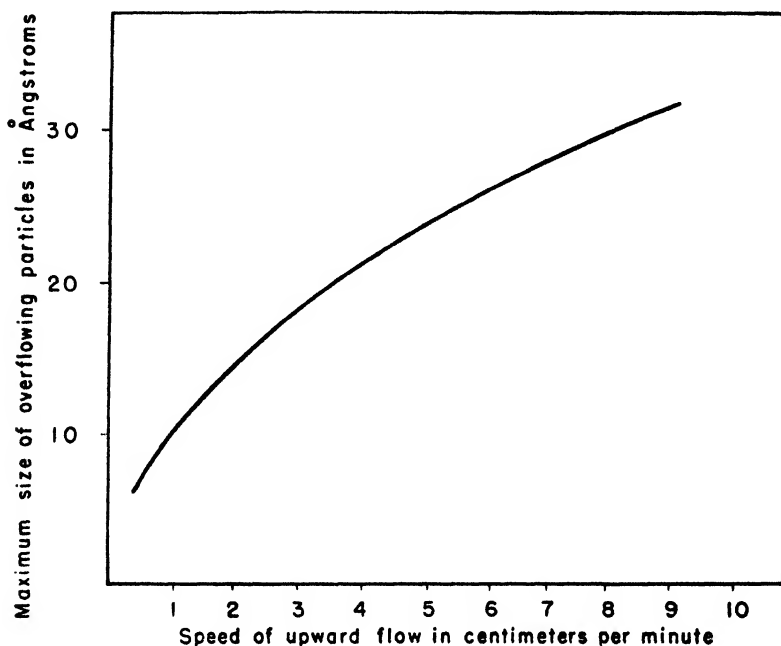
Figure 9. Relationship between maximum size of overflowing particles and speed of upward flow

Naturally, aggregates larger than the limiting value will fall to the bottom of the elutriation vessel. The horizontal axis shows the velocity of upward flow in centimeters per minute, and the vertical axis gives the size in microns of the largest entrained particles. Thus to obtain an overflow consisting of particles below the visible range, 6 microns, the elutriation speed has to be reduced to about one half centimeter per minute. These values correspond to separation at ordinary temperatures, 15° to 25° C., but at higher temperatures slightly greater speeds will produce the same operation. The sediment of larger aggregates is removed and reground in a pebble mill and again submitted to deflocculation and elutriation. On long standing the overflow will separate into a thick slurry and

a supernatant layer of clear water, but for practical purposes the separation can be speeded up by acidifying the suspension to a pH above 4, or by adding magnesium sulfate or other neutral salt with polyvalent anion. The dilution of the suspension has no very material influence upon the effectiveness of the process and is determined primarily by economic considerations.

In a specific application, a slurry of 20 tons of calcined titanium dioxide in 240 tons of water was dispersed with the requisite amount of sodium hydroxide and fed continuously over a period of 24 hours into an elutriation tank of circular shape equipped with revolving paddles and having an effective settling area of 175 square feet and a depth of 9 feet. The treatment was carried out at normal room temperature of 15° to 25° C., although the capacity of the equipment would be increased by operating at somewhat higher temperature. The slurry was introduced at the center of the tank, overflow from the sides was then conducted to a smaller settling tank, and magnesium sulfate solution was introduced to effect coagulation. After this step the suspension was passed to another settling vessel of about the same dimensions as that employed for elutriation where the pigment particles settled rapidly to a pulp containing 33 per cent solids. The velocity of upward flow in the elutriation tank was adjusted to one third centimeter per minute; at this speed aggregates of 6 microns or larger settled, and the overflow carried only particles below this range. After coagulation the thick, settled slurry was filter-pressed, washed, dried, and pulverized to break up any aggregates formed during drying. Pigments produced under such conditions yielded paint films of a perfectly mirror-like appearance.

According to a similar hydroseparation process,[77] titanium dioxide was dispersed by grinding in a slightly alkaline aqueous solution of pH 9 to 12. The most effective dispersing agents proved to be alkali metal hydroxides, silicates, and phosphates, although organic compounds known as wetting agents were successfully employed within a narrow range of hydrogen ion concentration. For instance, at a pH of 7.6, phenol and sodium sulforicinate yielded marked dispersion. Partial deflocculation was obtained by the use of alkali metal carbonates and aqueous ammonia, but compounds such as sodium sulfate, barium carbonate, and calcium hydroxide were of no value and generally promoted reflocculation. For a number of carefully controlled tests on a typical pigment at pH values of 8 to 10, sodium hydroxide was found to be the most effective agent, and only 0.11 per cent, based on the titanium dioxide, was required to yield perfect dispersion of a slurry containing 1 part solids in 6.8

parts of water. As a rule titanium dioxide is treated with potassium salts before calcination, and the proportion of such compound in the final pigment was found to have a decided influence on the deflocculation. Other important factors were the dilution of the slurry and the hydrogen ion concentration of the solution. For instance, in dispersing suspensions containing 400 g. per liter titanium dioxide which had been calcined with 1.5 per cent potassium bisulfate, maximum fluidity occurred at pH of 10, although there was little variation between values of 9.5 and 12. But at hydrogen ion concentrations corresponding to pH values below 8.5, the degree of deflocculation was so low that the suspension would not flow through the viscosimeter, as shown in the following table.

TABLE 10

RELATION OF VISCOSITY TO pH

pH of Solution	Viscosity of Slurry
8.5	Infinite
9.5	1.08
10.5	1.02
12.0	1.05

Thus the general requirements for satisfactory dispersion are that the pH should be between 9 and 12, and that soluble salts should not be present in any appreciable amount. As a rule, addition of dispersing agents beyond the optimum value caused reflocculation and injured the pigment rather than improved it. Such a suspension containing 160 g. to 170 g. titanium dioxide per liter was then fed into a decantation apparatus and the size of the particles carried over was regulated by the rate of flow. The overflow which contained particles up to the predetermined maximum size was collected in a vat and coagulated by adding magnesium sulfate, aluminum sulfate, or sulfuric or hydrochloric acid. After settling, the flocculated pulp was filtered, dried, and disintegrated. The coarser material (underflow) was fed back to the ball mill with a later charge of fresh pigment. By this method the grinding and separation of the pigment were carried out in a continuous operation and the smaller particles were not reduced to an undesirable fineness.

For example, in a continuous ball mill there was introduced a pulp consisting of 1000 kg. titanium dioxide and 1000 kg. water in which was dissolved 1500 to 2250 g. potassium hydroxide. The ground material was discharged as a slurry into a vat to which water

was added at such a rate as to reduce the concentration of the dispersion to 200 g. per liter solids, and at this stage 2 to 3 liters more of potassium hydroxide solution containing 750 g. per liter of the base was added in such a manner as to obtain the maximum degree of dispersion as determined by viscosity measurements. The product was run into a continuous decantation apparatus and the overflow containing 160 to 170 g. per liter titanium dioxide of fine particle size was collected in a vat, coagulated with magnesium sulfate, and allowed to settle. After filtration the solid cake was dried and disintegrated to yield a pigment of improved fineness and hiding power. The coarser material which settled to the bottom of the decantation apparatus was withdrawn in a continuous manner and returned to the ball mill.

To minimize the introduction of water-soluble compounds in the finished product and to increase its resistance to discoloration, calcined titanium dioxide was dispersed in dilute sodium hydroxide or sodium silicate solution and after hydroseparation the suspension was flocculated by adding an acid-reacting compound of a trivalent metal (aluminum sulfate) and barium hydroxide was added to neutralize the slurry.[78] The sulfate ion was precipitated as barium sulfate. Similar results were obtained by adding calcium acetate or barium acetate to precipitate the sulfate ions and flocculate the dispersed titanium dioxide.[79]

Coarser particles may also be removed from calcined titanium dioxide by a process based on elutriation of suspensions in acid media.[80] The pigment particles were dispersed by grinding in 1.3 parts of water containing 1 to 5 per cent (based on the titanium dioxide component) of an acid-reacting chloride of aluminum, zirconium, cerium, thallium, or thorium in their highest state of valence at pH between 0.5 and 5, depending upon the agent used. Of these, aluminum chloride gave the best results. This product was diluted with water to 100 g. titanium dioxide per liter to yield an extremely fine dispersion in which the smaller particles remained suspended while the larger aggregates settled out rapidly. After the coarse-grained material had settled, the suspension of the fine particles was separated by decantation or elutriation and treated with a coagulating agent such as magnesium sulfate or sulfuric acid to effect coagulation and precipitation. The pulp was then filtered, washed, dried, and disintegrated, and in some cases it was subjected to an additional dry milling to reduce the oil absorption value.

Pigments treated in this manner had uniform particles below the visible range and gave paint films with smooth, glossy surfaces.

The tinting strength, hiding power, oil absorption, and color were in no way impaired by this step in the processing. Such pigments were normally acidic, however, with pH values between 4 and 6, but to overcome this the pulp, before drying, was neutralized by adding alkali or alkaline earth metal hydroxides or carbonates.

To illustrate the process, a mixture of 150 kg. calcined titanium dioxide pigment in 200 liters of water containing 4 to 5 kilograms of aluminum chloride was ground in a ball mill and the resulting suspension was retained in a vat for 8 to 10 hours, after which the clear supernatant liquor containing 80 g. per liter aluminum chloride was separated and returned for mixing with another batch of pigment. The thick sediment was then diluted to 1500 liters and agitated to reestablish the dispersion. After standing for 3 to 4 hours the upper portion of the suspension was removed, free from larger aggregates, and containing 85 to 90 per cent of the original material. A solution of 800 to 1000 g. magnesium sulfate in 2000 g. water was added to coagulate the particles, and the precipitated pulp was filtered, washed, dried, and disintegrated. The coarse-grained residue from the decantation step was removed and reground with a later batch of pigment.

Somewhat better results were reported employing a basic chloride instead of the normal chloride [81] as dispersing agent.

According to a novel method developed by Eckels,[82] an aqueous suspension of calcined titanium dioxide was deflocculated by adding ammonium hydroxide and the wet-milled and hydroseparated dispersion was coagulated by adding carbon dioxide. In the subsequent drying operation the ammonium carbonate was volatilized so that the final product was free from soluble salts. Pigments prepared in this manner had improved water-wetting properties and were readily dispersed in aqueous media.

Calcined titanium dioxide was separated into fractions of different particle size by gravity methods or centrifuging after dispersion in water with the aid of a basic chloride of aluminum, cerium, thallium, zirconium, or thorium.[83] To hasten deflocculation the calciner discharge was wet ground with one of these agents. The coarse particles were allowed to settle and the aqueous suspension of the fines was separated and coagulated with magnesium sulfate or similar compound having polyvalent negative ions. Alternatively, the coarser particles were removed from the suspension by centrifuging. In either case the coarse particles separated were further ground and treated as before. The coagulated slurry of the

fines was filtered, washed, dried, and disintegrated according to conventional methods.

Precipitated titanic oxide was calcined to transform all particles smaller than the wave length of visible light into aggregates of distinctly larger size, and the product was then ball-milled in the presence of water to form a pigment suspension. This slurry was continuously centrifuged [84] under constant conditions of solids concentration and of effective centrifugal force to remove the coarser fraction. The finer particles were recovered from the suspension throughout the centrifuging operation by coagulation or settling, and yielded a titanium dioxide pigment of high opacity and uniform texture, while the coarse material was returned to the mill for further grinding. Pigments treated in this manner had constant particle size characteristics and thus gave paint films having smooth, glossy surfaces.

According to McKinney,[85] the wet-milling step in the manufacture of titanium dioxide pigment was improved to produce products of fine texture readily incorporable in paint and enamel vehicles and having a low sensitivity to water by grinding the discharge from the calciner in the presence of a relatively small proportion, 0.5 to 2 per cent, of one or more aluminates of the alkali metals such as sodium, lithium, or potassium. These agents were mixed dry with the titanium dioxide or added to the slurry as a solution. Best results were obtained by carrying out the grinding operation in a closed circuit with 0.1 to 0.7 per cent of the aluminate based on the solid component.

De Rohden [86] ground calcined titanium dioxide with an equal weight of dilute ammonium hydroxide solution and added water to the residual paste to obtain a highly dispersed product. Dispersions were also produced in aqueous emulsions of organic substances containing proteins,[87] such as water casein paints and rubber latex. Up to 2 per cent alkali metal hexametaphosphate or alkali metal pyrophosphate was incorporated with the dry pigment and the mixture was added to the emulsion of the organic agent, with agitation.

Suspensions of the finely divided pigment in aliphatic acids, ketones, and alcohols were prepared by employing a tannic acid product such as tannic acid or gallic acid,[88] or a halide of aluminum, cerium, thallium, thorium, titanium, or zirconium.[89] Of the latter group, aluminum chloride was found to be the most effective. According to Gurevich,[90] titanium dioxide forms fairly stable sus-

pensions in hydroxyethylcellulose salts, and semistable suspensions upon treatment with sodium sulfate Na_2SO_4 and additions of small amounts of potassium hydroxide.

As already pointed out, the wet milling and hydroseparation normally involve coagulation steps with the result that the product can be redispersed with considerable difficulty, if at all, and such pigments are thus unsuited for use in aqueous media, as, for example, in casein paints and paper. Pigments for such purposes are usually ground dry and do not contain the occluded coagulating agent. This is normally accomplished on a commercial scale in mills of the ring-roll type (Raymond) [91] or in jet pulverizers (mikronizers).[92] Regardless of the type of milling, the pigment is passed through disintegrators or pulverizers of the rotary-hammer type and airfloated to insure the desired degree of fineness. The coarse material is returned for further grinding.

Composite pigments, because of their heterogeneous nature and the relatively large particle size of the extender or filler as compared with that of the titanium dioxide, are in general not amenable to the wet-milling and hydroseparation process such as is employed with the relatively pure oxide. Those products are normally subjected to dry-grinding operations as, for example, in mills of the ring-roll type or in jet pulverizers. They are likewise air floated to such a degree that not over 0.05 per cent will be retained on a 325-mesh screen, and they are then disintegrated or pulverized.

Treating the finely divided pigment particles with a nonaqueous wetting agent more volatile than the vehicle and compatible with it facilitated dispersion.[93] The agent was removed from the mixture during the kneading operation. Composite pigments readily dispersed in organic media may be produced by milling with 0.05 to 0.9 per cent naphthenic acid or calcium naphthenate as an added step.[94] Dispersion characteristics were also improved by treating the pigment with 0.1 to 1.0 per cent of a water-soluble glycolate.[95] Berry [96] produced composites free from particles of 5 microns and larger for direct use as mix-in pigments in paints and enamels. From 0.03 to 4.5 per cent of a polar-nonpolar compound (oleic acid, naphthenic acid) was intimately mixed with a finished titanium dioxide-calcium sulfate pigment, and the treated product was dispersed in a current of air and subjected to a classification treatment to remove the coarse particles. Calcined pigment was treated with 0.1 to 5.0 per cent zinc, calcium, or magnesium resinate, abietic acid, phenolic resin, or fatty acids, pulverized in an air stream, separated

and repulverized to reduce the particle size and improve the texture.[97]

The presence of water greatly increases the viscosity of paints and enamels containing the calcium sulfate composite pigment. This effect, known as bodying, may be lowered by adding alkaline compounds to the composition or it may be increased by adding acidic compounds. Aliphatic amines were found to be particularly effective in lowering this bodying tendency.[98]

Oil-Absorption Characteristics and Gloss

In the manufacturing process, oil absorption of the pigments is affected by the nature and amount of the conditioning agents incorporated with the hydrous oxide and by the calcination conditions themselves. Potassium carbonate or sulfate is the primary compound employed, and as the proportion is increased the oil absorption is reduced. However, the use of increased quantities of these agents is often harmful to other properties, particularly color, tinting strength, and fineness. Oil absorption of the finished pigment may be further reduced by a dry-milling process but this is effective to a limited extent, and the method is naturally more applicable to varieties having abnormally high initial oil values since in any case a minimum is reached which may again increase on further grinding. Prolonged milling may also injure the color and other pigment properties.

To determine the oil absorption value, 3 g. of the finished pigment is weighed onto a glass plate and refined linseed oil just short of the estimated amount required is added from a burette. The components are thoroughly mixed by working slightly with a spatula, and more oil is added, drop by drop, until the powder is thoroughly wetted and the whole mass becomes plastic. After the end point is reached, the addition of one drop more will cause the paste to smear on the glass. Results are converted to parts of oil by weight required per 100 parts of pigment, and this number is known as oil absorption.

From a practical standpoint, oil absorption too high results in coating compositions (paints) that are too thick and have impaired gloss, while oil absorption too low results in thin paints which tend to sag or run, subsequent to application. These difficulties, resulting from variations in this property, can be corrected in general by reformulation of the paint, but this procedure is inconvenient and

costly to the manufacturer and he naturally prefers a uniform product.

Pigments of lower oil absorption characteristics and increased covering power were reported to be obtained by incorporating a small proportion of sodium hydroxide, sodium nitrate, sodium sulfate, or the corresponding potassium compounds, aluminum sulfate, or magnesium sulfate in hydrolytically precipitated titanic oxide before calcination.[99] These accelerators could be formed *in situ* during the hydrolysis step and did not exceed 10 per cent of the titanium dioxide, but in general 0.5 to 1 per cent produced optimum results. Calcination was carried out at 900° C. and the product was ground and pulverized according to accepted practice.

Rhodes[100] found that calcining the hydrous oxide with from 0.1 to 2.5 per cent, on the dry basis, of an alkali metal titanate (potassium titanate), which would not discolor at the temperature employed, yielded a pigment of lower oil absorption as well as higher opacity and improved mixing properties (dispersion). Later work revealed that similar results could be obtained by employing 1 to 2.5 per cent of an alkaline earth metal titanate.[101]

According to McKinney,[102] oil absorption may be varied willfully over wide limits in the manufacturing process by treating the washed pulp with small proportions of alkali metal salts (potassium sulfate) together with phosphoric acid or phosphates so that the calcined product will have a mole ratio of alkali metal to phosphorus within the range of 1 to 1 and 1.6 to 1. For example, if a high value is desired, the hydrous oxide is calcined with from 0.2 to 0.4 per cent potassium sulfate, while on the other hand calcination with from 0.7 to 3 per cent of this addition agent gives a product having a low value. Pigments within the normal range are obtained by employing from 0.4 to 0.7 per cent potassium sulfate. The alkali metal-phosphorus ratio is held, however, between the range of 1 to 1 and 1.6 to 1. Ilmenite, the chief raw material used in pigment manufacture, normally contains phosphate compounds which are converted to the soluble form in the digestion step. During hydrolysis the phosphate constituent is mostly adsorbed by the precipitate of titanic oxide, and only a small proportion, if any, is removed in the washing operation. In calculating the required ratio, the residual phosphate is included in the total.

This treatment prevents the formation of hydrated titanic acid subsequent to calcination by decomposition of titanates and phosphates. Hydrated titanic acid has a detrimental effect upon the color of baked alkyd resin films, and it is acted upon by certain

vehicles and converted to blue or gray titanous compounds that cause discoloration of the system. Furthermore, titanium dioxide pigments produced in accordance with this process have good fineness and are particularly free from coarse particles.

In an example, washed hydrolytically precipitated titanic acid was slurried to 390 g. per liter solids and analyzed for phosphorus pentoxide. Allowing for losses of potassium sulfate during the subsequent filtration and slight losses of phosphorus pentoxide during calcination, the necessary amount of potassium sulfate was added to produce a mole ratio of 1.17. The slurry was then dewatered in such a manner as to produce a cake containing 40 per cent titanium dioxide and 0.53 per cent potassium sulfate, based on the solid component, and the product was calcined to produce a pigment containing 0.3 per cent phosphorus pentoxide and 0.53 per cent potassium sulfate, and having a pH of 7.3. The calciner discharge was dispersed, ground, flocculated, and filtered. The dewatered cake containing 60 per cent titanium dioxide was dried at 150° to 170° C. in a continuous steam-heated rotary drier and disintegrated in a mill of the hammer type to produce finished titanium dioxide pigment.

With a constant potassium content, low mole ratios (high phosphorus) resulted in low oil absorption, but as the ratio was increased by lowering the phosphorus content the oil absorption increased rapidly to a maximum and fell off, at first rapidly and then more gradually, as the mole ratio was further increased. With extremely low mole ratios resulting from high phosphate content, color and tinting strength tended to be poor.

The oil absorption of pigments processed by the conventional methods, that is, calcined at 900° to 1000° C., ground wet in a ball mill, passed through a hydroseparator to get an average particle size of 0.5 micron, dried, and pulverized, was greatly reduced by a dry pulverization process [103] in which the pigment particles were subjected to considerable pressure or momentary impact. At the same time other pigmentary qualities were likewise improved. This effect was accomplished by hand grinding a few grams in a mortar, or on an industrial scale by grinding the pigment in a dry condition in a Raymond mill or chocolate mill. In normal plant operation a grinding period of from 1 to 2 hours was required. The oil absorption of pigments subjected only to wet milling (35 to 55) was reduced to 25 or less by this additional dry-grinding process, and the higher the original value the greater was the proportionate reduction by milling. This operation had the additional advantage

of increasing the hiding power of the pigment, as determined by the cryptometer, by 5 to 10 per cent, and it also increased the tinting strength up to 20 per cent.

This marked reduction in oil absorption values by dry-milling processes cannot be ascribed to actual reduction of the primary particle size since the particles are far too small to be affected by the grinding action.[104] The effect can be explained, however, as an agglomeration of the pigment into compact particles which are not readily penetrated by the vehicle. In fact this has been demonstrated experimentally. Booge[105] attributed the reduction in oil absorption to some change in the surface or adsorption characteristics of the pigment particles. According to a method reported by Barton,[106] the pigment, after conventional wet milling, drying, and disintegration, was submitted to a high pressure without grinding or attrition to reduce the oil absorption. The size of the pigment particle was not reduced appreciably by the treatment.

From a study of the quantity of water taken up by titanium dioxide pigments at various intervals, the rate of wetting[107] was found to depend upon the size, shape, and kind of particles and upon the volume of pores, but influence of size and shape disappeared on compacting the material under pressure. The amount of oil absorbed paralleled that of water.

Finely divided pigment free from aggregates and possessing low oil absorption was produced by subjecting calcined titanium dioxide to a pulverizing type of milling followed by a disintegrating type of milling.[108] Pigments ground by the conventional wet-milling process have oil absorption of from 24 to 26, and lower values are desired in many paint and enamel formulations. Substantial reduction of this value may be obtained by a pulverizing process in which the particles are subjected to considerable pressure. Commercial ring-roll mills are preferred for this purpose, and in practice these are ordinarily equipped with an air-separation system which depends on centrifugal force to separate the coarse particles and return them to the mill for further pulverizing while allowing the fines to pass on as finished product. Such a treatment reduces the oil absorption by around 25 per cent from 24 to 26 to 17 to 20. However, this reduction is accompanied by a sacrifice in texture, and an increase in grittiness of the pigment. This decrease in texture is attributed to the compacting action of the pulverizing process so that many particles of titanium dioxide are pressed together in the form of flakelets or pellets and these persist as coarse aggregates or grit. This is a logical explanation of the unusual effect, in that

vigorous pulverizing does not produce an impalpable powder but tends to coarsen the pigment and produce grittiness rather than finer texture.

Another type of dry milling is by disintegrating, such as may be accomplished in rotary-hammer mills, but this operation applied to titanium dioxide does not produce a fine subdivision of the coarse particles formed during the calcination process, nor does it reduce pigment oil absorption. However, it does break up flakes or pellets produced by compacting.

By employing these processes in series, the beneficial effects of both were imparted to the pigment. The ring-roll mill broke up hard pigment grit and reduced oil absorption, while the rotary-hammer mill broke up the relatively soft aggregates formed during the ring-roll milling. The pigment was first subjected to pulverizing milling in a ring-roll mill of 50-inch diameter equipped with an air-separator system which separated the coarse particles from the fines, returned the coarse material for further grinding, and discharged the fines. At this stage the pigment contained an undesirable quantity of aggregates and was passed to disintegration milling in a rotary-hammer mill of 24-inch diameter. The pigment passed through the dry-milling equipment at the rate of 1600 to 2300 pounds per hour.

Sawyer [109] employed a series of grinding operations. The calcined pigment was first subjected to a grinding operation in a high-pressure, fluid-energy mill with steam at a temperature of 300° to 500° C. under a pressure of 50 to 150 p.s.i., and the product was passed through a closed-circuit, wet-grinding system equipped with a hydroseparator. The overflow was coagulated, dried, and disintegrated in a low-pressure, fluid-energy mill to break up agglomerates formed during the drying operation.

Parravano and Caglioti [110] concluded from a theoretical consideration that rutile modification of titanium dioxide should have a slightly higher oil absorption than anatase. The unit cell of anatase contains twice as many molecules as that of rutile, with the result that a unit weight of the former material has a smaller surface area.

Oleaginous coating compositions pigmented with calcium sulfate-extended titanium dioxide tend to exhibit poor gloss and poor gloss-retention characteristics. That is, they produce films having an undesirably dull, matte appearance, which for some uses is objectionable. This property was improved by adding to the pigment between 0.1 and 1 per cent benzenecarboxylic acid or an equivalent amount of one of its salts. [111] Furthermore, pigments treated in this

manner possessed improved wetting, mixing, and dispersion properties in oil, varnish, and other vehicles without an increase in consistency. They had superior tint retention, higher resistance toward discoloration and yellowing, and reduced sensitivity to water. Such pigments in organic coating compositions did not settle to a hard dense cake on standing, and the aged material produced films which dried as rapidly as freshly prepared products. In an actual operation, benzenecarboxylic acid was added to a 70 per cent calcium sulfate-30 per cent titanium dioxide pigment at the rate of 15 pounds per hour while the pigment was being fed at the rate of 3000 pounds per hour into a 50-inch ring-roll mill equipped with an air separator. After treatment and pulverization in this manner, the pigment was disintegrated by passing it through a 24-inch rotary-hammer mill, also at a rate of 3000 pounds per hour.

Sutton [112] obtained better gloss characteristics by intimately mixing with the pigment a small proportion (0.5 per cent) of a trialkylphenyl or trialkylphenylalkylene ammonium hydroxide. Similarly, gloss and hardness values were improved by mixing with the calcined titanium dioxide, in aqueous suspension, a small proportion of water-insoluble basic compounds of cobalt such as the hydroxide.[113] The treated product was dried and pulverized.

According to Brill,[114] composite barium sulfate base pigments, to which had been intimately mixed 0.05 to 5 per cent of an agent such as the barium salt of a sulfonated aromatic petroleum derivative, did not cake in oil vehicles and produced a paint of unimpaired gloss and flow properties. It should be remembered, however, that with any given pigment the gloss characteristic of the film varies inversely with the ratio of pigment to vehicles in the composition.

Pigments of high surface-hiding power were produced by forming on the surface of the individual particles a coating of gel-like polymeric carbohydrate compound.[115] With an aqueous suspension of calcined and ground titanium dioxide was mixed 0.25 to 0.35 per cent, calculated as polyhydric carbohydrate and based on the weight of pigment, of an alkaline solution of a polymeric carbohydrate derivative such as cellulose xanthate, and dilute sulfuric acid was added to bring the pH of the system to below 7, thereby precipitating the agent in gel-like form on the surface of the titanium dioxide particles. The mixture was dewatered, and the cake was dried at a temperature not in excess of 200° C.

A pigment free from grit particles [116] was produced by heating a slurry of calcined titanium dioxide containing 0.2 to 10 per cent of an added salt (calcium chloride) or an acid or base for at least

30 minutes at a temperature above 100° C. If acid or alkali was used, the slurry was neutralized after digestion. This treatment rendered soluble certain cementing agents, and the high temperature served to dehydrate any gelatinous material, thereby preventing it from having a cementing action on the pigment during the subsequent drying operation. Such gelatinous material could result from the hydrolysis of alkali metal titanates which may have been formed during the calcination step. In an example, 10,000 parts by weight of calcined titanium dioxide pigment which had been wet ground and elutriated under alkaline conditions, coagulated with magnesium sulfate, and adjusted to a pH of 7 with sulfuric acid, was allowed to settle to slurry concentration of 400 g. per liter. This was diluted with water to 150 g. per liter and 10 per cent or 1000 parts of hydrochloric acid was added, after which the slurry was brought to boil and held with agitation for 2 hours. It was then cooled to 70° C. and filtered. The cake was washed with water at the same temperature by displacement and reslurried to 150 g. per liter solids. After standing for 16 hours the suspension was neutralized with sodium hydroxide, filtered, and washed. This cake was dried at 175° C. and disintegrated in a high-speed hammer-type pulverizer.

Chapter 15

CHALKING AND DISCOLORATION

Paint, enamel, and lacquer films, pigmented with regular (unmodified) titanium dioxide alone, in outdoor service usually exhibit a type of rapid failure known as "chalking," [1] which manifests itself as a tendency of the surface layer to disintegrate to a powdery chalk. As this material is removed by the eroding action of wind and rain the underlying section is exposed to further attack so that the wearing away is progressive. The powdery surface assumes an unpleasing dull appearance and tends to collect dirt and mildew. In mixtures with coloring agents to form tinted coating compositions, titanium dioxide prepared by ordinary methods produces a whitish chalk on the surface of the tinted film upon exposure to atmospheric conditions, thereby producing an unsightly and faded appearance.

Furthermore, such pigments incorporated in compositions with organic dyestuffs frequently accelerate fading of the added color, particularly on exposure to sunlight. However, by blending the titanium dioxide with pigments of the chemically active type such as zinc oxide and white lead, the degree of chalking can be minimized and controlled. At the same time the types of failure characteristic of the reactive pigments, such as checking and cracking, are greatly reduced or eliminated altogether.

On the other hand, coating compositions pigmented with titanium dioxide do not exhibit this objectionable property of chalking in indoor service, but tend to discolor, characterized by a progressive yellowing of the film.

Many methods have been proposed for producing titanium dioxide pigments free from these limitations, and considerable progress has been made toward a solution. The most common practice is to incorporate with the hydrous oxide before calcination small proportions of conditioning agents such as antimony trioxide, zinc oxide, and rare earth compounds, or to coat the individual particles of titanium dioxide after calcination with small amounts of such agents as hydrous alumina, chromic oxide, silica, and zirconium compounds, or combinations of these. Such treatments increase the resistance to chalking, discoloration, and fading to an appreciable

extent, but in some cases at some sacrifice in color, brightness, and tinting strength. The alumina treatment is particularly effective in overcoming the tendency toward discoloration.

Various explanations have been offered to account for this poor resistance to chalking, but no theory has yet been advanced which could account for all or even most of the known facts. This phenomenon occurs only in the presence of solar radiation, and moisture is also an important factor.[2] Some authorities hold that it is the result of lack of molecular or other contact or attrition between the so-called nonpolar pigment particles and the vehicle. This would appear to be only a secondary factor, however, since films of this type last indefinitely in indoor service. Thus the primary cause for destruction of the loose contact appears to be solar radiation not necessarily in the visible range.

Resistance to actinic light appears in many cases to be a function of the atomic weight and of the size of the molecules of the various pigment materials. Metallic lead, for instance, is impervious to X rays, while aluminum with a very much lower atomic weight is transparent. Barium sulfate containing barium, an element of high atomic weight, is also relatively impervious, in contrast to sodium sulfate or even calcium sulfate. Pigments containing lead compounds, as for example the carbonate, are more resistant than those consisting of compounds of the lighter metals having lower atomic weights, and similarly polymerized linseed oil with a large molecule gives more resistant films than does the untreated material. As an analogy, these factors may be interpreted as meaning that the destructive rays have to be stopped by an armor plate of high atomic weight or by a "sandbag" containing a multitude of smaller atoms.

According to this hypothesis, titanium with a relatively low atomic weight of 48 should not be resistant to radiation, but it is exceptional in having a very high index of refraction. Radiant energy falling on a moderately opaque film is reflected gradually from the particles throughout the whole depth of the film, but the same radiation hitting a highly opaque film pigmented with titanium dioxide is reflected more from the surface layer, and the shock of impact must therefore be borne by a relatively small number of particles containing a metal of low atomic weight. Thus it appears reasonable that titanium dioxide alone may never be so resistant as lead pigments in a linseed oil vehicle.

Two methods of overcoming this difficulty suggest themselves. The first is to employ titanium dioxide, along with other pigments

having a high atomic weight, either in chemical combination or as a mechanical mixture. Lead titanate, for example, is little affected by solar radiation. In a study of mixtures of titanium dioxide with carbonates of barium, strontium, and calcium, the resistance to chalking of the composite pigments was found to be of the same order, showing that the compound containing the metal of high atomic weight was superior. The second method, employing vehicles of high molecular weight such as bodied linseed oil, also gave good results in practice.

Wagner [3] concluded that the initial destruction of a paint film is due to the action of ultraviolet light on the oil and that chalking appears later. Water, if present, penetrates the disrupted surface, causing swelling, and thus accelerates the complete destruction. Both these defects are related to the oil absorption of the pigment, and fine grinding should be avoided. Maximum durability is obtained from compositions in which neither the pigment nor any soap formed from it by reaction with the vehicle undergoes hydrolysis. Further improvement may be obtained by sealing with dispersed fillers the pore spaces of pigments having low swelling power.

Chalking has also been ascribed to the inactive nature [4] of the titanium dioxide. In preparing coating compositions, surface active pigments such as zinc oxide, basic lead carbonate, and iron oxides become an inherent part of the oil gel and give dense impervious films while the inactive pigments as titanium dioxide produce films which are more porous and more easily penetrated by water. Films of this type naturally tend to fail more readily by chalking, and consequently show poor tint retention.

Zhukova and Sovalova [5] concluded that such disintegration is caused by instability of the system titanium dioxide-linseed oil to atmospheric action, which in turn is the result of inertness and poor wettability of solid particles in the vehicle. The system can be so stabilized as to prevent the chalking by the addition of soaps such as barium oleate and sodium salts of linseed oil fatty acids, which by forming pigment-enveloping aggregates facilitate dispersion in the oil. Fillers such as nephelite, talc, and barium carbonate are effective in retarding chalking of the composite films since these form dipolar compounds with the vehicle and thus favor the formation of adsorption aggregates.

According to another hypothesis, the chalking of films pigmented with titanium dioxide is ascribed to the action of atmospheric factors on the oil of the vehicle, catalyzed by the titanic oxide.[6] The process is inhibited by covering the surface with a second layer

containing another and more stable pigment. Alternatively the same favorable results may be obtained by coating the particles of the commercial pigment with an adsorbed layer of aluminum hydrate, ferric hydroxide, zirconium oxide, and other nonpigment material before suspending them in the oil vehicle. Lyophile substances such as aluminum soaps are not effective.

Some authorities have suggested that pigments which absorb strongly in the ultraviolet should show good resistance to chalking failure, since their absorption would shield the organic constituent of the film from this harmful radiation. Such a theory is lent credence by the relatively low ultraviolet absorption of regular titanium dioxide. However, on the other hand, some of the special grades, for instance those treated with small proportions of antimony oxide, alumina, and zirconium compounds, and possessing normal tinting strength, have practically the same absorption characteristics but widely different chalking resistance. According to an explanation by Rubin,[7] the action of ultraviolet light on drying oils produces peroxides and these oxidize the titanium dioxide to pertitanic acid, which in turn oxidizes the oil of the film to produce chalking. Rutter [8] carried out experiments with titanium dioxide pigmented paints on glass and concluded that the chief cause of breakdown was the oxidation of the medium with the pigment acting as catalyst. Rutile proved more resistant to weathering than the anatase modification.

To develop a rapid test for chalking, experiments were carried out with aniline blue FF which is rapidly destroyed in the presence of titanium dioxide by ultraviolet rays.[9] The products of oxidation are weakly colored so that the photosensitizing action of the pigment may be judged from the extent of fading.

In normal calcination practice the pigment is subjected to a temperature of 900° to 1000° C., depending upon the exact nature of the original material and the properties desired in the final product. The intensity of the calcination is a function of both the temperature employed and the time of exposure, and although some properties improve progressively with the severity of this treatment, others increase to a maximum value and then fall off. For instance, the tinting strength of the resulting pigment increases with the intensity of the calcination to a maximum value and then decreases, while on the other hand there is a progressive improvement in the ability of the pigment to give stable and durable coatings in the usual paint vehicles. If calcination is intensified to increase the tinting strength to the fullest extent, there is a tendency for the pigment to acquire a

grayish, yellowish, or reddish tone and often a lack of fastness to light. A still further increase in the degree of calcination to obtain a product that will show great resistance to chalking in paint films normally results in a drop in tinting strength and the material becomes excessively hard so as to render it unsuited for normal use in coating compositions.

Pigments of particularly good durability, brightness, stability, and fastness to light may be obtained by incorporating from 0.1 to 20 per cent antimony trioxide with the hydrolysis product before calcination,[10] although 1 per cent of this agent gave optimum results. In general, the antimony can be more conveniently added as a suspension of the trioxide, although water-soluble compounds (potassium antimony tartrate) may be employed. The principal advantage gained by using the relatively large proportion of antimony is that the intensity of the calcination may be increased so as to enhance the chalking resistance of the resulting pigment without excessive hardness, but on the other hand the degree of brightness resulting from the use of small proportions of this conditioning agent is not always reached, although the tone is usually attractive and varies from pure yellow through neutral white to bluish. The neutral and bluish tones are obtained under particularly intense conditions of calcination. Although the titanium dioxide with the higher proportions of antimony compounds can be calcined at higher temperatures than were formerly possible without causing excessive hardening, the tinting strength of the product will not always be the maximum value and may be lower than could be obtained at a lower temperature. For many purposes, however, it is more important to produce a pigment that yields films of high durability than one having the maximum covering power.

Improvements in the softness of the pigments and the durability of films are noticeable with an amount of antimony trioxide as low as 0.1 per cent of the titanium dioxide, and there is a progressive improvement in these properties as the proportion is increased to about 20 per cent. With proportions above this value the product again hardens and tends to assume a grayish to greenish tone. Under some conditions, antimony trioxide, even in very small amounts, has a tendency to impart a bluish cast to the pigment. By employing an equivalent amount of the pentoxide a less pronounced tone is obtained without adversely affecting the other properties.

A careful study of the reactions involved indicated that the antimony combines with the titanium dioxide to form an antimony-titanium-oxygen compound which is practically insoluble in water,

dilute acids, and alkalies. This conclusion is substantiated by the fact that the full amount of antimony added appears in the finished pigment, although the calcination temperature was much higher than that at which antimony oxide would normally be volatilized. Further improvement in the softness of the calcined pigment may be effected by adding the antimony compound along with other conditioning agents, such as potassium carbonate, but phosphoric acid and phosphates in general tend to counteract the beneficial effect of the antimony and should be used with care if at all. This process is also applicable to the production of other pigments in which titanium dioxide is an important constituent as composites and titanates.

Although the antimony compound is normally mixed with the washed pulp, it may be added at any earlier stage of the process; for instance, the trioxide or tartar emetic may be added directly to the titanium salt solution prior to the hydrolysis step. Such compounds may be mixed with the titanium ore before it is reacted with sulfuric acid and the antimony will remain in the solution and precipitate along with the titanium. According to another modification, the antimony compound is mixed with an already calcined titanium dioxide pigment and the mixture is subjected to a second calcination. Regardless of the method, the antimony compound must be thoroughly and uniformly incorporated with the titanium oxide.

In an example, thoroughly washed hydrous titanium oxide pulp obtained by hydrolytic precipitation was intimately mixed with 1 per cent antimony trioxide and 0.4 per cent potassium carbonate, based on the titanium dioxide, and calcined at 980° C. The product was white with a neutral tone and had a high fastness to light. It was very soft, and in ordinary vehicles gave films of great durability in outdoor service. All the antimony originally added was retained in the calcined product, indicating that combination had taken place.

Similarly, titanium dioxide pigment, calcined at a temperature above 900° C. with 0.1 to 10 per cent of an oxide of lead or a compound that yields the oxide under the conditions employed, showed improved stability and weather resistance.[11] To improve resistance to chalking, Pall[12] calcined titanic oxide, hydrolytically precipitated from sulfate solutions, first in a reducing atmosphere and then in an oxidizing atmosphere. Additional improvements were obtained by treating the pulp with potassium carbonate as well as with 0.01 to 0.03 per cent ferric oxide and 0.0004 to 0.0025 per cent copper before calcination. By calcining gamma titanic acid under different conditions with varying proportions of zinc oxide, the product consisted of zinc titanate with titanium dioxide in the anatase or rutile form

or in solid solution.[13] Such pigments had excellent hiding power and resistance to chalking. Pigments of rutile type possessing superior color, brightness, and resistance to light and weathering were produced by carrying out the calcination in the presence of minor proportions of an alkali metal compound and a water-soluble compound of a metal having a valence greater than 1, such as aluminum, zinc, magnesium, and beryllium.[14]

Pigments of markedly improved resistance to chalking and fading were produced on a commercial scale by heating a mixture of titanium dioxide with approximately 1 per cent zinc oxide or an equivalent amount of other compounds of zinc at 850° to 1050° C. until the crystal structure, as determined by X-ray examination, showed a large proportion of rutile.[15] Employing anatase titanium dioxide as the starting material, better results were obtained if the hydrous product was preliminarily calcined in the usual manner to develop first such desired pigmentary properties as tinting strength, color, and oil absorption, and then recalcined with zinc oxide to convert the crystal structure to the rutile form and impart the durability characteristics. The zinc component appeared in the final product as the titanate. Finished pigments were characterized by uniform relatively coarse particle size. This method was also applicable to normal pigments of rutile type such as those obtained from chloride solutions, and also to calcium sulfate, barium sulfate, and other composites. In an actual operation, 100 kg. of previously calcined anatase titanium dioxide was suspended in water to a volume of 400 liters, and a solution of zinc sulfate containing the equivalent of 1 kg. of the oxide was added, with vigorous agitation. The slurry was evaporated to dryness, calcined for 30 minutes at 950° C. in a rotary kiln, wet-ground, filtered, dried, and pulverized. Examination showed that 90 per cent of the titanium dioxide had been converted to rutile; its average particle-size diameter was 0.45 micron; and color and tinting strength approached those properties of the standard pigment. Peterson [16] found that after proper treatment the same results were obtained with a single calcination. To an aqueous slurry of hydrolytically precipitated anatase titanium dioxide was added 0.5 to 0.75 per cent of a mixture of potassium sulfate and sodium sulfate and 0.25 per cent zinc sulfate. The product was heated at 975° C. until conversion to rutile was practically complete as determined by X-ray examination. At the same time the desired pigment properties were developed. Aluminum sulfate, magnesium sulfate, and barium sulfate could be substituted for the zinc sulfate.

Ancrum [17] produced a pigment of the rutile type, having improved brightness and whiteness, by incorporating with the hydrous oxide before calcination potassium silicate corresponding to 0.25 per cent potassium oxide and 0.18 per cent silica, based on the dry weight. Similar improvements were obtained by adding an insoluble white silicate.[18] The finely divided rutile form of titanium dioxide was suspended in water, and the treating agent was precipitated in place by the reaction between sodium silicate and the water-soluble metallic compound. From 2 to 5 per cent of the insoluble silicate gave optimum improvement.

Titanium dioxide pigments of the rutile crystal form, having very high durability and resistance toward chalking and fading in paint films, were produced by a two-stage calcination involving conversion from the anatase modification at elevated temperatures.[19] Hydrous titanium oxide, as obtained by the hydrolysis of sulfate solutions, was first calcined in the usual manner to develop pigmentary properties in the presence of such negative catalysts as alkali metal compounds which inhibit or retard rutile crystallization. The product obtained was recalcined after removing the added agent to effect conversion to the rutile crystal form and at the same time develop the property of resistance to chalking. From 0.3 to 1.0 per cent of the alkali metal compound (potassium sulfate), based on the weight of the pigment, was required in the first calcination, but in the second the proportion of this agent was reduced to below 0.1 per cent. The compound was removed during the usual washing and filtering operations normally employed in pigment manufacture. This process was also applicable to composite pigments.

In an example, hydrous titanium oxide was calcined in the presence of 0.5 per cent, based on the weight of the titanium dioxide, of potassium sulfate at a temperature of 985° C. to form anatase titanium dioxide having good pigment properties such as color, tinting strength, and oil absorption. This product was dispersed in water with 0.18 per cent sodium hydroxide and ground in a pebble mill to break up aggregates. The aqueous slurry was coagulated with magnesium sulfate, approximately 0.25 per cent, neutralized with sulfuric acid to a pH of 7, and filtered, dried, and pulverized. This finely divided pigment was then subjected to a second calcination at 1000° C. for several hours to develop the rutile crystal modification. At the same time the size of the crystals increased. The product of this second calcination was in a finely divided form, and after being ground by wet or dry methods was suitable for direct use in coating compositions. Average particle-size diameter ranged from 0.35 to

1.8 microns, but the major portion of the pigment was within the range 0.40 to 0.80 micron.

Farup [20] developed a process of coating the individual particles of titanium dioxide with insoluble compounds, for example oxides, hydroxides, and sulfates of aluminum, zinc, and lead, as a protection against destructive external influences, without at the same time materially impairing their pigmentary values. This treatment rendered the pigment more resistant to physical and chemical changes and prevented discoloration of paint films on exposure to light and heat. The coating was effected by precipitating the desired compound directly on the titanium dioxide particles from an aqueous solution in which the pigment was suspended. Suitable precipitants were sodium carbonate, sodium hydroxide, ammonium hydroxide, and a soluble white sulfate. Since only a small proportion of the protecting material was necessary to effect stabilization, larger amounts were used only to modify the inherent characteristics of the pigment.

In a typical operation of the process, calcined titanium dioxide was finely ground and suspended in water. A concentrated solution of aluminum sulfate was added in amount to yield alumina equal to 2.0 per cent of the suspended pigment, and after mixing thoroughly, aqueous sodium carbonate was added to precipitate the aluminum as hydrous oxide. Agitation was continued until the reaction proceeded to completion. The solid product, consisting of particles of titanium dioxide covered with hydrated aluminum oxide, was washed thoroughly, dried, and pulverized to yield a pigment stable against the action of weathering, heat, and light.

In a modified method of applying the coating, a suspension of the pigment in a solution of aluminum sulfate containing the equivalent of 1 per cent of the oxide based on the titanium dioxide was heated to 80° C. and agitated for 16 hours, after which the temperature was again brought to 80° C.[21] Ammonium hydroxide solution was then added to raise the pH to 7.4, and agitation was continued for an additional 2 hours. The coated pigment particles were filtered, dried at 130° C., and pulverized. By another procedure, a suspension of the pigment, a solution of aluminum sulfate, and aqueous sodium carbonate were introduced simultaneously into a reaction vessel.[22] Seidel [23] treated an aqueous suspension of calcined titanium pigment with 2 per cent (on the solid basis) of a soluble compound of titanium and of aluminum or chromium, and adjusted the pH to 7 to effect precipitation. The treated product was washed, dried, and pulverized.

Patterson [24] produced a pigment having high stability and improved resistance to weathering, discoloration, chalking, and lack of tint retention by blending separately prepared and washed hydrous aluminum oxide with a slurry of calcined and ground titanium dioxide. This process had the advantage over methods by which the alumina was precipitated in the presence of suspended particles of pigment, in that it avoided the introduction of soluble salts into the product during the treatment. Similar improvements in properties were obtained by exposing finely divided titanium dioxide to vapors of aluminum chloride at a temperature above 300° C.[25] Enamels pigmented with this product did not darken on exposure to ultraviolet light. Because of the adsorptive nature of such pigments, the soluble salts cannot be completely removed by washing, and unless these are reduced to extremely low proportions, 0.25 per cent, they exert an injurious effect upon the durability of exterior paints and coating compositions in which the pigment is employed.

Alumina of the desired quality was prepared by adding an alkaline agent to a solution of aluminum sulfate, with agitation in the cold, until the mixture was neutral as determined by pH measurements. The precipitate was washed free of soluble salts by decantation or filtration and blended as an aqueous slurry with a suspension of the titanium pigment. To obtain uniform incorporation of the components, the suspension was agitated thoroughly, after which the treated pigment was filtered, dried, and pulverized. Maximum benefits were in general obtained by applying 1 per cent of the agent to the titanium dioxide, although amounts from 0.1 to 2 per cent were employed to suit individual requirements. There are numerous uses for which treated pigments are not required, and it is apparent that several different products can be prepared from the same batch of raw pigment.

In an example, 15 parts by weight of crystalline aluminum sulfate was dissolved in 250 parts water, and dilute ammonium hydroxide was added slowly, with agitation, until the pH of the slurry was brought to 7.0 to 7.2. The precipitated hydrated aluminum oxide was then washed by decantation and filtration to remove soluble salts, after which it was slurried in water to 250 parts by weight. This suspension was added to a water slurry of 230 parts calcined and ground titanium dioxide, and after thorough mixing the treated pigment was filtered, dried, and pulverized in the conventional manner.

Precipitation and washing of the alumina were carried out in the cold, and the product was not allowed to dry before use, otherwise its effectiveness was greatly diminished. Better results were ob-

tained by blending the agent immediately after precipitation with the pigment slurry.

Hanahan and McKinney [26] precipitated hydrous alumina upon titanium dioxide pigments by reacting aluminum sulfate with an alkaline earth metal hydroxide, the sulfate of which was insoluble in water. Pigment produced in this manner was practically free from soluble salts and showed improved resistance to chalking, discoloration, and fading of tint. A solution of aluminum sulfate was added to a water suspension of titanium pigment, and the pH of the slurry was brought to 7 by adding, with vigorous stirring, an equivalent amount of barium hydroxide solution. This resulted in precipitation of the aluminum on the surface of the pigment particles in the form of hydrous oxide and at the same time the sulfate was converted to insoluble barium sulfate. The slurry was then filtered, and the pigment was dried and pulverized for use in coating compositions. Alumina content of the final product ranged from 0.02 to 2 per cent, but in general 1 per cent gave optimum results.

The resistance to chalking and discoloration was also increased by suspending the calcined and finely divided pigment particles in an aqueous solution of an alkali metal aluminate and allowing it to remain until a small amount of an aluminum compound was adsorbed by or on the individual pigment particles. [27] According to a more direct method, a neutralizing acid (sulfuric) was added to the solution to decompose the aluminate and precipitate the aluminum hydroxide on the particles, after which the suspension was heated at 70° to 90° C. for 3 to 5 hours. The coated product was filtered, washed, dried, and pulverized. In an example, 1 kg. calcined titanium dioxide was ball-milled for 2 hours at room temperature with 3 kg. of a sodium aluminate solution containing the equivalent of 10 g. aluminum oxide, 1 per cent, based on the titanium dioxide. The aluminate was prepared by adding sodium hydroxide to a solution of aluminum sulfate to precipitate the hydroxide, and an additional amount to redissolve the precipitate. After milling was completed, the slurry was discharged into a suitable vessel, diluted to 15 per cent solids, and heated for ½ hour at 80° C. The titanium dioxide thus coated with alumina was separated from the liquor, washed to remove the sodium sulfate, dried, and pulverized.

Similar results may be obtained by stirring the calcined and ground titanium dioxide in a solution of a basic aluminum salt such as a highly basic chloride, formate, or acetate. [28] Pigment particles treated in this manner acquired a coating of aluminum oxide and showed improved resistance to weathering and discoloration. Basic

aluminum chloride was prepared by dissolving freshly precipitated aluminum hydroxide in aluminum chloride solution or by adding sodium carbonate to an aluminum chloride solution. Composition may be expressed according to the degree of substitution, for instance, Al_2Cl_5OH, $Al_2Cl_4(OH)_2$, and $Al_2Cl_2(OH)_4$. According to a specific operation, 10 parts by weight of titanium dioxide pigment was stirred for 3 hours at room temperature with 80 parts by weight of a clear 0.10 per cent solution of highly basic aluminum chloride containing 1 mole of chloride for each 2 moles of aluminum. The suspension was then filtered, washed, and dried.

Krasnovskii and Kiselev [29] added oxides of aluminum, zinc, magnesium, calcium, and barium to increase the resistance to chalking and discoloration. The improvement increased with ionic radius of the oxide.

Hanahan and McKinney [30] suspended calcined titanium dioxide in a solution of barium aluminate and added aluminum sulfate to precipitate small proportions of aluminum hydroxide and barium sulfate on the individual pigment particles. Similarly, a pigment suspension was mixed with a solution of aluminum acetate and calcium hydroxide was added to precipitate a basic aluminum acetate compound and acetic acid was added to neutralize the solution exactly.[31] Surface coatings of hydroxides of aluminum, antimony, tin, or bismuth were deposited effectively upon the surface of the pigment particles by hydrolysis of the corresponding chloride, formate, arsenate, propionate, or butyrate solution.[32]

A pigment consisting of a mixture of titanium dioxide and hydrated or anhydrous alumina gave paint films of superior whiteness and improved resistance to chalking.[33]

Gardner [34] found that the chalking resistance could be improved by coating the particles with inorganic cementation substances such as hydraulic cement, hydraulic lime, or plaster of Paris. After dispersing the calcined titanium dioxide in a slurry of the coating material, the system hardened by hydration and the solidified mass was crushed and powdered to obtain a particle size suitable for use in film-forming coating compositions.

Pigments suitable for external use were prepared by suspending calcined and ground titanium dioxide in dilute aqueous solutions of salts (sulfates) of the rare earths, of tetravalent compounds of titanium, zirconium, hafnium, thorium, and cerium, and precipitating the hydroxide or hydrated oxide on the suspended particles in such a manner as to fill and seal the interstices or pores of the original material.[35] Precipitation was accomplished by hydrolysis on

boiling the solution or by adding sodium carbonate, ammonium hydroxide, potassium hydroxide, or a similar agent, with vigorous agitation. Alternatively the coating or filling material was added to a suspension of the pigment in water as a colloidal oxide or hydroxide and deposited on the individual particles of titanium dioxide by adding a coagulating agent or by evaporating the water. After neutralization of any residual acid, the mixed product was dried and calcined at a red heat. For example, 10 parts by weight of finely ground calcined titanium dioxide was suspended in 100 parts of a solution of titanyl sulfate containing the equivalent of 200 g. per liter of the dioxide. The mixture was then heated to effect hydrolytic precipitation of the titanium as hydrous oxide on the suspended particles, and the pore-filled product was separated from the solution, washed, and calcined at 800° to 1000° C.

Robertson [36] coated the pigment particles with 2 to 5 per cent of a silicate of zirconium, aluminum, magnesium, cerium, zinc, or barium to improve the resistance to weathering and to discoloration. In an example, calcined titanium dioxide was slurried in a solution of basic zirconium chloride and aqueous sodium silicate was added as the precipitating agent. Similar improvements were obtained by coating the titanium dioxide with a small proportion of an alkali metal silicate. [37] A slurry of the pigment was mixed with sodium silicate, and barium chloride was added to precipitate barium silicate.

Kinzie [38] coated or impregnated the individual particles of titanium dioxide with small proportions of the oxide or silicon complexes of zirconium to increase the resistance to chalking. The zirconium compound was incorporated with the hydrous titanic oxide or with calcined material, but in either case the mixture was calcined to develop the desired properties. Proportions of the added agent were employed, expressed as the oxide, from 0.5 to 5 per cent of the base pigment, but values of 1 per cent in general gave optimum improvement.

Calcined titanium dioxide pigment was treated with a relatively small proportion (below 5 per cent) of a silicon complex such as sodium zirconium silicon citrate, zirconium silicon chloride, or sodium zirconium silicon chloride, and the mixture was lightly calcined to 700° C. On heating the mixture, zirconium oxide and silicon oxide were formed in the same proportions in which they occurred in the complex, $ZrSiO_4$. The sodium chloride remained as such and was removed by washing. According to another variation of the process, calcined pigment particles in suspension were treated with zirconium sulfate solution in a predetermined proportion, and

phosphoric acid was added to precipitate the zirconium as phosphate. The mixture was simply washed to remove any residual acid, dried at 110° C., and pulverized in the usual manner. With appropriate modifications the treatment was found to be applicable to hydrous titanium oxide.

Increased durability in outdoor service was developed by coating the individual particles with fluorides that were soluble only with difficulty.[39] This treatment was effected by precipitating the fluoride compound directly onto the pigment, or by suspending the titanium dioxide in a solution of a complex fluoride, e.g., a salt of fluosilicic acid, H_2SiF_6, and heating the mixture to convert the complex into the corresponding fluoride. For instance, finely divided pigment was stirred into aqueous ammonium fluoride containing magnesium chloride or a 40 per cent fluosilicic acid solution, and aqueous ammonium or barium hydroxide was added to effect precipitation, whereby the individual particles were coated with basic magnesium fluoride or with barium fluorosilicate, according to the method followed. The product was filtered, washed, and pulverized.

Patterson[40] prepared a pigment characterized by high resistance to chalking and discoloration by coating the individual particles with 1 to 10 mole per cent of cadmium oxide, hydroxide, or carbonate. According to a typical operation, 4000 parts by weight of regular pigment-grade titanium dioxide was suspended in 16,138 parts of an aqueous solution of 183 parts cadmium chloride. The mixture was agitated until a smooth slurry was obtained, and 80 parts of sodium hydroxide, dissolved in 720 parts of water, was added to precipitate all the cadmium as hydroxide; this compound remained attached to the pigment particles. After thorough mixing the suspension was filtered, washed, dried, and disintegrated to obtain a product containing 2 mole per cent of cadmium hydroxide. The treated pigment was a fine white powder, and paint films pigmented with it exhibited excellent resistance to chalking in outdoor service and to progressive yellowing in indoor use.

Addition of titanium phthalate[41] was found to increase the chalking resistance and also to retard the rate of fading of organic dyes adsorbed on the pigment on exposure to sunlight. This agent was made by adding a titanium salt solution, adjusted to a slight acidity, to aqueous sodium phthalate prepared by neutralizing phthalic acid or anhydride with sodium hydroxide. One mole of phthalic acid reacted with 2 moles of alkali, and the resulting salt reacted with ½ mole of titanic sulfate. A dense white precipitate formed, which usually contained more or less titanium oxide, depending upon the

degree of hydrolysis. On drying at 105° C. the phthalate became gelatinous and showed a tendency to form semivitreous or horny aggregates resembling silica gel or a hard resin. Because of this property, better results were obtained by precipitating it directly upon suspended particles of titanium dioxide, and the dried material consisted of individual pigment particles coated with a semivitreous shell of titanium phthalate. Linseed oil paints, enamels based on phenolic-tung-oil varnishes, or alkyd resin vehicles and nitrocellulose lacquers pigmented with this composite product showed greatly improved resistance to chalking and color fading as compared with equivalent untreated pigments. From 5 to 10 per cent of the titanium phthalate gave the maximum improvement in these properties. The phthalate did not have any great degree of opacity, however, and thus contributed relatively little to the hiding power of the coating composition.

The most important factor in the destruction of films is ultraviolet radiations; pigments which transmit such radiations allow them to penetrate the film and destroy the binder. On the contrary, pigments which are relatively opaque to these rays should give films possessing good resistance to chalking and tint retention. The fact that titanium phthalate transmits none, or a very small proportion, of ultraviolet light may be one of the reasons for its unusual weathering property. Furthermore, dry titanium phthalate absorbs small proportions of moisture, and it is possible that the durability of films pigmented with this compound results from the flexibility imparted by the absorbed water. Tint failures in lacquers may be overcome by incorporation of titanium phthalate, since it appears to shut out the radiations that cause disintegration of the lacquer film.

Coating compositions of this type were prepared by grinding 30 parts of the phthalate-treated pigment in 70 parts of a tung-oil spar varnish containing a modified phenol-formaldehyde resin or 25 parts of the pigment in 75 parts of an alkyd resin varnish. A characteristic lacquer was obtained by dispersing 10 parts of titanium phthalate, incompletely dried from alcohol, in 90 parts of a solution of 10 parts cellulose acetate in a mixture of 20 parts of cellosolve acetate and 60 parts of acetone. Ten parts of methyl phthalate was added as plasticizer.

Titanium phthalate, on the other hand, contributed little to the durability of clear varnishes.[42]

The phthalate (and in fact all titanium salts of organic polybasic acids) retards the growth of mildew and other destructive organisms on cellulosic films and filaments and has the additional property of

minimizing the transmission of ultraviolet radiations into the interior.[43] Dispersed throughout cellulosic filaments, films, bands, or masses in small proportions, the phthalate imparts a soft, translucent, "delustered" appearance, and still larger proportions render the composition opaque.

As an example of actual operation, 296 g. phthalic anhydride was dissolved in boiling water and 160 g. sodium hydroxide was added gradually to form a practically neutral salt. This solution was added slowly to approximately 1405 ml. of a slightly acid titanium sulfate solution equivalent to 80 g. of the dioxide and containing per liter 57 g. titanium dioxide, 140 g. combined, and 62 g. free sulfuric acid. The white, extremely finely divided precipitate, almost colloidal in appearance, was filtered and washed, but before drying alcohol was passed through the product to displace the water. On evaporation of the alcohol a very finely divided fluffy white pigment was obtained which did not contain fritted particles. Acidity of the titanium sulfate solution was an important factor. If it was highly acid, precipitation was delayed and the yield and composition of the product were unsatisfactory. On the other hand, a practically neutral solution gave a precipitate containing an appreciable proportion of hydrous titanium oxide. Commercial titanic sulfate solutions are often extremely acid, and if used were partially neutralized, e.g., by adding aqueous sodium hydroxide. Although small proportions of free titanium oxide in the precipitate were permissible, large percentages tended to promote yellowing of paint films on exposure to the atmosphere.

In preparing a treated pigment of this type, 2000 g. regular calcined titanium dioxide was suspended in 10,000 g. of water, and 1000 g. of slightly acid sulfate solution containing the equivalent of 42.5 g. titanium dioxide was added. Separately, 160 g. phthalic anhydride (a slight excess) was dissolved in 3000 g. of water containing 87 g. sodium hydroxide and poured gradually into the suspension with the result that titanium phthalate precipitated immediately on the surface of the pigment particles. Thus, approximately 200 g. titanium phthalate was precipitated on 2000 g. regular titanium dioxide and after thorough agitation the product was washed, dried, and pulverized.

To a cellulose xanthate jelly such as is used in the manufacture of films, there was added titanium phthalate equivalent to 6 per cent of the cellulose content. After thorough mixing this composition was extruded through slits to form sheets which were then passed through precipitation and washing baths and finally dried in the conventional

manner. These films were quite opaque to ultraviolet radiations, but had a sufficient degree of transparency to visible light to make them attractive in appearance.

Similar improvement in the chalking resistance of titanium dioxide pigment was obtained by coating the individual particles with from 1 to 10 per cent of a basic titanium phthalate having approximately the composition indicated by the formula $C_8H_4O_4 \cdot (TiO(OH))_2 \cdot \times H_2O$.[44] In carrying out the process, a solution of titanyl sulfate was first prepared. Commercial titanium sulfate cake containing the equivalent of 20 per cent titanium dioxide and 50 per cent sulfuric acid was dissolved in an equal weight of water at about 60° C. The cooled solution was treated with lime slurry to neutralize one third of the total sulfuric acid, and the calcium sulfate formed was filtered off. The filtrate was then analyzed and sodium hydroxide solution was added to adjust the titanium dioxide-sulfuric acid ratio to that corresponding to titanyl sulfate ($TiOSO_4$). Titanium dioxide pigment was suspended in the clear solution and a $\frac{1}{2}$ mole proportion of aqueous sodium phthalate was added to precipitate the basic compound on the individual particles. The proportions were so adjusted that the final washed and dried pigment contained 3.5 per cent of the coating compound. Although the basic titanium phthalates contained 40 to 50 per cent titanium dioxide, they possessed very little hiding power and were of a brownish color. From 0.5 to 2.5 per cent of a polysubstituted derivative of phthalic acid, such as dialkyl or diphenyl phthalate, also proved effective.[45]

A pigment composition consisting of titanium dioxide intimately associated with from 0.5 to 10.0 per cent of an insoluble salt of a metal from Group III or IV of the Periodic Table with a saturated, dibasic, aliphatic acid containing at least three carbon atoms to the molecule gave paint films having high durability and improved resistance to chalking and fading.[46] The more effective acids of the group were found to be malonic, succinic, glutaric, adipic, and pimelic. In a typical operation, 1000 parts by weight of calcined and ground titanium dioxide pigment was suspended in 6000 parts of water, and 89 parts of titanic sulfate in 300 parts of slightly acid solution was added. To the agitated mixture was then introduced a separately prepared solution of 66 parts succinic acid dissolved in water containing 45 parts sodium hydroxide. The titanium succinate, approximately 100 parts, precipitated immediately on the surface of the pigment particles, and after thorough agitation the composite product was filtered, washed, dried, and pulverized for use in film-forming coating compositions.

These desirable chalk- and fade-resistant properties were also obtained by mixing regular titanium dioxide pigment with a small quantity of a dibasic acid or anhydride at any stage of the manufacturing process following calcination.[47] Phthalic acid and anhydride were found to be the most efficient agents of the group.

Titanium phthalate, as well as that of zinc, lead, barium, or cadmium, was reported to compare favorably with zinc oxide as pigment except for a slight reddish cast.[48] They were characterized by relatively high oil-absorption and bulking value; they gave good body to paints and tended to produce products of a thixotropic nature; they had a soft texture and were easy to grind.

New [49] observed that the addition of 3 per cent chromium oleate to paints pigmented with titanium dioxide greatly increased the stability of the resulting films. In some tests the period of exposure to weathering required to cause chalking to reach a standard value was doubled. The effectiveness of the oleate or resinate of tin was less conclusive, for although 3 per cent of these agents showed a similar improvement with one paint, no improvement was detected with another of similar composition. Beneficial results were also obtained by treating the pigment particles with the chromium compound before incorporation into the vehicle.

The resistance to weathering of paint films containing titanium dioxide was improved by incorporating a small proportion of an oxidizing agent such as a peroxide or per salt of an alkali or alkaline earth metal (barium peroxide) which was capable of liberating hydrogen peroxide by reaction with the acid of the vehicle.[50] Neutralizing agents, such as oxides, carbonates, or hydroxides of zinc, magnesium, and aluminum were also added for this purpose. The resistance of titanium dioxide pigments to the action of light and atmospheric agencies was improved by heating them in alkaline solutions as an added step in the manufacturing process.[51]

Goodeve [52] observed a sharp drop in the reflecting power of titanium dioxide and zinc oxide at 400 and at 385 millimicrons, respectively. These oxides were reported to be a source of photoactivation for the oxidation of oil vehicles or for the bleaching of adsorbed dyes, and the action of each was specific. For example, titanium dioxide promoted oxidation of linseed oil while zinc oxide did not. From these data Goodeve ascribed the reduction of chalking by zinc oxide to inner filter action.

Acicular zinc oxide mixed with titanium dioxide pigments was particularly effective in arresting chalking without cracking.[53] Jaeger [54] added 5 per cent zinc oxide to a titanium dioxide pigment

containing 2.5 per cent combined phosphoric acid to prevent disintegration of the resultant paint film on outside exposure. Similar results were obtained by adding 5 to 25 per cent of this agent to relatively pure titanium dioxide or alkaline earth sulfate base composites.[55] A nonchalking pigment consisting of 5 to 25 per cent titanium dioxide and 75 to 95 per cent zinc carbonate was obtained by adding sodium carbonate to a suspension of finely divided calcined titanium dioxide in a zinc sulfate solution, with continuous agitation.[56] The composite precipitate was washed, dried, and pulverized.

Titanium dioxide in combination with other pigments, particularly zinc oxide and white lead, is sufficiently resistant to weathering for use in outdoor service. By striking the proper balance of the components, the rate of chalking may be cut down to the point where it becomes desirable, in that the resulting paint films become self-cleansing to a degree not before attained and thus maintain a clean, bright surface.

White pigments consisting of titanium dioxide of the rutile crystal form together with zinc orthotitanate proved quite resistant to chalking.[57] Fillers and extenders could be included in the composition. The mixture was heated at 840° C. to effect combination with the zinc oxide to form the titanate and to convert the unreacted titanium dioxide to the rutile modification as determined by X-ray examination. Part of the zinc could be replaced by magnesium. Large quantities of anatase were transformed to rutile with a small proportion of zinc, since the titanium dioxide seemed to pass through the titanate stage and then break up to yield rutile and zinc oxide to form more titanate. As an illustration of the process, 1 part of zinc oxide was intimately mixed with 3 parts of titanium dioxide of anatase type and heated for 12 hours at 900° C. The product was a white pigment consisting of zinc orthotitanate with 60 mole per cent rutile, and it possessed good covering power and resistance to disintegration on weathering. In another example, a mixture of hydrous titanium oxide and barium sulfate, containing 25 per cent titanic oxide on the dry basis, was heated with 7 per cent zinc oxide for 10 hours at 900° C. to produce a chalk-resistant pigment consisting of zinc orthotitanate, rutile, and barium sulfate.

The discoloration or progressive yellowing of films pigmented with unmodified anatase grade of titanium dioxide in indoor service has been ascribed to the formation of peroxide linkages at the unsaturated double bonds in the drying oil of the vehicle.[58]

Incorporation with the titanium dioxide, after calcination, of 0.02 to 1.5 per cent precipitated beryllium oxide or hydroxide inhibited

discoloration in baked enamels.[59] Similar improvements were effected by incorporating 2 to 3 per cent elemental molybdenum[60] of 150-mesh particle size, and by coating the pigment particles with 0.002 to 2.0 per cent chemically precipitated cobalt oxide.[61]

Pigments coated with aluminum oxide produce a minimum of discoloration in resin vehicles under conditions of both air drying and baking. In fact, such films actually bleach on exposure to diffused light.

Titanium oxide pigment treated with 0.5 to 10 per cent of a metal salt of a water-soluble, relatively volatile organic acid was found to impart to paint films color stability and improved resistance to chalking and weathering.[62] Salts of aluminum, zinc, cadmium, beryllium, magnesium, calcium, barium, and strontium with acetic, formic, propionic, butyric, citric, and oxalic acids were particularly effective. Aluminum acetate, for example, is quite unstable in solution and can be readily hydrolyzed by heating, thereby depositing relatively insoluble basic aluminum acetate on the surface of suspended pigment particles.

In actual operation of the process, 4000 g. of ground pigment was mixed with 3500 ml. of solution containing 183 g. zinc acetate. The paste was thoroughly mixed to break up aggregates and to procure a uniform distribution of the components, after which it was dried, and the product was pulverized in a hammer mill.

Titanium dioxide pigments, in association with chromium naphthenate, possessed markedly reduced chalking and fading characteristics.[63] The chromium naphthenate was applied as a surface coating to the pigment particles or by mixing chromium naphthenate into the film-forming composition pigmented with titanium dioxide. In the former the pigment was suspended in an aqueous solution of an alkali metal naphthenate, and water-soluble chromium chloride or sulfate was added. Thus by double decomposition there was precipitated on the suspended particles a coating of chromium naphthenate. Proportions of 0.2 to 5 per cent were used, although the lower limit usually gave the desired results.

The resistance to fading, chalking, and loss of gloss-retention of titanium dioxide in paint films was appreciably improved by coating the individual particles of the calcined pigment with very small amounts of hydrous oxides of both aluminum and chromium.[64] Furthermore, dyed artificial fibers delustered with such a pigment showed good light resistance and color retention. Between 0.05 and 0.15 per cent chromium oxide and between 0.5 and 1.5 per cent aluminum oxide, both in the hydrated form and based upon the

weight of the pigment, gave optimum results, and these agents were added directly to the suspension or precipitated in place. The pH of the suspension was then adjusted to a value of 6 or 8 by adding a neutralizing agent, and the mixture was heated to 60° to 90° C. and held at this temperature, with stirring, to insure an intimate association of the components. Subsequently the slurry was dewatered and the pigment was dried at a temperature not over 250° C. and dry milled.

In a typical operation, a 20 per cent aqueous slurry of the calcined wet-milled titanium dioxide was heated to 75° C. and solutions of aluminum sulfate and chromium sulfate equivalent to 1.0 per cent and 0.1 per cent, respectively, of the corresponding oxides on the pigment basis were added. The mixture was maintained at a temperature of 80° to 90° C. and stirred continuously for 2 hours. At this stage heating was discontinued, and ammonium hydroxide was added with agitation until a pH of 7 was attained, thereby precipitating the aluminum and chromium as hydrous oxides on the surface of the pigment particles. The suspension was agitated for an additional hour, after which it was filtered and the treated product was dried at 160° C. and disintegrated by passage through a rotary-hammer mill.

The beneficial effect of some of these agents was found to be additive. A combination of 0.05 per cent chromium, as oxide, 2.0 per cent zirconium silicate, and 1 per cent alumina, separately precipitated upon the particles of calcined titanium dioxide, was very effective in increasing the resistance to chalking and to discoloration.[65] .The colored chromium oxide did not impair the brightness of the finished pigment.

Chapter 16

COLORED TITANIUM DIOXIDE AND TITANATE PIGMENTS

Colored Pigments

Titanium dioxide pigments of distinctive colors and tints may be [1] produced by calcining the hydrous oxide, as obtained by thermal hydrolysis of ilmenite solutions, with small proportions of compounds of the heavy metals having atomic numbers between 50 and 64 inclusive, such as vanadium, chromium, iron, cobalt, nickel, manganese, and copper. Chromium and vanadium are particularly effective for the main reason that their power of imparting color to the resulting pigment is exceedingly strong; only very small amounts of these agents are required to produce distinct colorations. Such products consist of particles of titanium dioxide containing a small amount of a heavy metal compound (usually oxide) physically or chemically associated therewith. Colors obtainable range from the extreme of red to the other extreme of green, through such shades or tints as grays, buffs, yellows, light browns, and tans. These pigments have the valuable properties of straight titanium dioxide and differ in chemical properties and constitution from titanates. The small amount of colored compounds does not adversely affect the tinting strength, chemical resistance, or particle size of the straight titanium dioxide which forms the basis of the pigment. On the other hand, the phenomenon of fading in paint films is greatly decreased or eliminated altogether. Resistance to chalking is greatly improved, and if the products chalk on excessive exposure, the film is colored and not conspicuous. This property is so pronounced that the tinted products protect white pigments or extenders with which they are mixed in controlled amounts. Tinted pigments of this type are composed of particles which under the microscope appear homogeneous and show the same color throughout, and for this reason they are readily distinguished from mechanical mixtures of the components.

In general the desired tints are obtained within the range of 0.3 to 7 mole per cent of the heavy metal compound. Chromium and

vanadium form notable exceptions, however, in that less than 0.3 mole per cent is sufficient to produce distinct colorations. The colors imparted to the final pigment by the different addition agents are tabulated below.

TABLE 11

COLORS OF TINTED PIGMENTS

Compound Added	Color in Linseed Oil
Chromium nitrate $Cr(NO_3)_3 \cdot 9 H_2O$	Light gray tan
Chrome alum $Cr_2(SO_4)_3 \cdot K_2SO_4 \cdot 24 H_2O$.	Buff
Potassium dichromate $K_2Cr_2O_7$	Dark buff
Cobaltous nitrate $Co(NO_3)_2 \cdot 6 H_2O$	Gray ivory
Cupric nitrate $Cu(NO_3)_2 \cdot 3 H_2O$	Light green with very slight yellow cast
Ferric sulfate $Fe_2(SO_4)_3 \cdot 9 H_2O$	Cream
Potassium permanganate $KMnO_4$	Pink fawn
Nickel nitrate $Ni(NO_3)_2 \cdot 6 H_2O$	Ivory with light green cast
Solution of vanadium pentoxide, V_2O_5, in hydrochloric acid	Gray

Normal calcination at around 950° C. was generally sufficient to develop the pigment properties, although higher temperatures, for example up to 1250° C., were used. In many instances beneficial results were obtained by carrying out the calcination in the presence of water vapor.

In an example, 100 ml. of a solution containing 7.77 g. potassium carbonate and 10 ml. of a solution containing 2.18 g. potassium chromate were separately added to 3 liters of washed pulp containing 900 g. titanium dioxide. These proportions represented 1 mole per cent potassium as the carbonate and 0.1 mole per cent chromium, or 0.86 per cent potassium carbonate and 0.24 per cent potassium chromate by weight of the final product. The mixture was stirred and set aside for 16 hours to allow the added salts to become intimately mixed with the particles of titanium dioxide. It was then filtered and the resultant wet cake was heated in a rotary calciner to 950° C. in 45 minutes and held at this temperature for 30 minutes. The light buff colored product obtained was ground to produce a pigment of the desired texture. Another sample prepared in exactly the same manner, except that 35 ml. of potassium chromate solution containing 7.63 g. of the salt was added, had a medium buff color. Such titanium compounds were mixed with barium sulfate, calcium sulfate, china clay, silica, or silicates to produce tinted composite pigments.[2]

Better products were obtained by calcining an intimate mixture of hydrous titanium oxide and the tinting agent (compounds of chromium, cobalt, nickel, vanadium, and manganese) at a temperature of 450° to 1050° C. in an atmosphere containing at least 25 per cent of steam by volume.[3]

Coffelt[4] prepared colored titanium dioxide base pigments containing a small proportion of chromium in the form of a chromate. The desired amount of this agent was coprecipitated along with the titanium during the hydrolysis step, or added later to the filtered and washed pulp and the mixture was heated to form titanium chromate. Pigments having a light yellow to dark buff tint were produced by calcining a mixture of titanic oxide, a compound of antimony, and a compound of nickel or cobalt.[5]

Titanium oxide base pigments tinted through cocalcination with a minor amount of a chromium compound were stabilized by digestion in the presence of 0.05 to 10 per cent by weight of an oxidizing agent such as hydrogen peroxide, sodium perborate, or ammonium persulfate for a period of time sufficient to convert all the chromium present to the hexavalent state.[6] Pigments processed in this manner had a yellow to buff color with relatively clear undertones and showed improved resistance to change of tint or color on exposure to light and air. Furthermore, they formed paints characterized by improved resistance to fading and chalking.

Gray pigments of predetermined and improved shade and subordinate tint were produced by calcining an intimate mixture of hydrous or precalcined titanic oxide with 0.1 to 2 per cent vanadium, as a convenient compound, and a potassium salt equivalent to 0.3 to 3 per cent of the element, in an atmosphere containing 0.1 to 2 per cent carbon monoxide at a temperature between 800° and 1025° C.[7] If the pigment was cooled rapidly, a blue-gray color was obtained, while slow cooling yielded a yellowish undertone. At the proper intermediate rate of cooling, a neutral gray tone was produced. Specifically, cooling in air to 400° C. in 2 seconds to 5 minutes gave a bluish cast; from 5 minutes to 1 hour, a neutral gray tone; and from 1 hour to 5 hours, a yellow undertone.

According to a related procedure, buff titanium dioxide pigments of predetermined and improved shade and subordinate tint were produced by calcining an intimate mixture of titanium pigment with 0.02 to 2 per cent, calculated as the element of a chromium compound, and 0.3 to 3 per cent of a potassium salt in a carbon monoxide-free atmosphere for a period of not more than 5 hours, and thereafter in an atmosphere containing carbon monoxide for a

period of not more than 2 hours at a temperature between 800°
and 1025° C.[8] The pigment was cooled in an oxygen-containing
atmosphere free from carbon monoxide.

In the regular method for thermal hydrolysis of titanic sulfate
solutions, the chromium component, acquired from the ore or added,
is almost completely precipitated along with the titanium and the
desired amount of this agent was effectively mixed with the hydrous
titanic oxide by this method.

Mixtures of titanium dioxide crystallizing in the tetragonal form
with the sesquioxide crystallizing in the corundum type of the
rhombohedral form were found to possess good pigment properties.
Products containing several tenths of a per cent of titanous oxide
had a bluish tone, and the intensity increased with higher propor-
tions of this component and varied through blue to black. By
replacing part or all of this agent by sesquioxides of aluminum,
chromium, iron, vanadium, and rhodium, which also crystallize in
the corundum type, various colors were produced: for example,
black, gray, blue, yellow, orange, or white.

In preparing pigments of this type, titanium dioxide was mixed
with titanous compounds or their solutions and heated to 800° to
1100° C. in nonoxidizing conditions. Similarly the dioxide was
mixed intimately with the corresponding amount of aluminum,
chromium, iron, vanadium, or rhodium, as metallic powders, and
heated in the absence of oxygen to bring about the reaction. In an
example, 20 kg. of a paste of titanic oxide containing 14 per cent
water was slurried with 20 liters of a sulfate solution containing 2
kg. of titanous oxide, and the mixture was dried and heated at 900°
to 950° C. for 1 hour under nonoxidizing conditions to form a
pigeon-blue pigment.[9]

To produce differently colored pigments, Goldschmidt [10] reduced
titanic oxide with carbon. The product was thought to be a solid
solution of titanium sesquioxide in the dioxide. Blue pigments in
which all the titanium was in the trivalent state [11] were prepared by
heating amorphous titanium dioxide with a carbonaceous reducing
agent at 800° to 1000° C. Crystallization of the oxide was pro-
moted by adding to the initial mixture from 0.5 to 5 per cent of
zinc oxide or ammonium fluoride. Titanium pentoxide produced by
the high-temperature reduction of ilmenite was treated with calcium
fluoride and sulfuric acid, or heated with calcium fluoride and am-
monium fluoride, to volatilize the silica as tetrafluoride.[12]

Passerini [13] calcined hydrous titanic oxide with metallic salts in
such proportions as to form approximately equimolecular amounts

of the corresponding titanate and an isomorphous metal compound. The characteristic color resulted from the formation of solid solutions of the two types of compounds formed. For example, ferrous oxide, stannous oxide, magnesium oxide, and titanium dioxide, on calcination, gave a yellow-brown solid solution of $FeSnO_3$ and $MgTiO_3$. Similarly, copper oxide, aluminum oxide, zinc oxide, and titanium dioxide gave a violet-colored solid solution of $Cu(AlO_2)_2$ and Zn_2TiO_4.

A paste of finely ground ilmenite and zinc sulfate in sulfuric acid was heated to 950° C. and the reaction product was calcined for 2 hours at 800° C. in an atmosphere composed of equal parts of carbon monoxide and carbon dioxide to produce a black pigment.[14] The composition had a base of titanic oxide and the iron component served as the coloring agent.

Ryan and Cauwenberg [15] calcined a mixture of powdered ilmenite and lead oxide, carbonate, or acetate, under oxidizing conditions at 800° to 1000° C. until the reaction was complete, to produce a reddish brown pigment composition containing lead titanate and ferric oxide. All ferrous oxide was converted to ferric during the process. By varying the ratio of constituents and the calcination conditions, a variety of colors was obtained.

An anticorrosive composition [16] was produced by grinding titanium black (rutile) and lead cyanamid in linseed oil, and a green pigment [17] was obtained by mixing cobalt chromate with magnesium titanate.

The sludge remaining after leaching the reaction product of ilmenite and sulfuric acid with water was neutralized with an alkali and washed with water, dried, calcined, and ground to form a brown pigment containing titanium dioxide.[18] Zinc oxide was used to neutralize part of the residual acid and thereby introduce this component into the final composition.

Hager [19] produced titanium dioxide pigments having a blue tint by coating the surface of the particles with a minor amount of hydrous oxide of trivalent titanium. To a suspension of regular calcined and ground pigment was added an aqueous solution of trivalent titanium equivalent to between 0.005 and 1.0 per cent, calculated as the element and based on the weight of titanium dioxide. The suspension was neutralized with alkali and the composite product was washed, dried, and pulverized. The residue obtained by evaporating the filtrate from hydrolysis of ilmenite solution was ignited to drive off the sulfur trioxide, mixed with calcium carbonate, and calcined to yield a pigment consisting of calcium sulfate

together with calcium titanate and calcium ferrite.[20] A violet to black crystalline solid suitable for use as pigment was prepared by heating magnesium with titanium dioxide, metallic titanium with magnesium oxide, or titania and magnesia under reducing conditions.[21] Colored titanium oxide-containing pigments have been produced from clays rich in this constituent.[22] The matrix was washed out and the residue was ignited to burn out organic matter, treated with acids to remove the iron compounds, and finally washed, dried, and pulverized.

Goldschmidt [23] colored titanium dioxide with organic dyes such as crystal violet, nigrosin, and eosin. The original pigment particles were suspended in water and stirred with the coloring agent until complete adsorption took place, after which the product was dried and pulverized. This general procedure was also followed by Blumenfeld.[24] Titanium dioxide pigments have been used as bases for the production of lakes from dyes such as paranitranilin reds and toluidine reds.[25] Titanium tannate and ferrocyanide can be used for yellow and green pigments, respectively.[26]

Titanate Pigments

Goldschmidt [27] prepared pigments, in which all or part of the titanium was combined in the form of crystalline titanates, by heating to sintering or fusion a mixture of hydrous titanium dioxide with oxides, hydroxides, or carbonates of calcium, strontium, barium, magnesium, lead, zinc, manganese, and other bivalent base metals. These products were insoluble in water and very stable against both oxidizing and reducing agents, so that in paint films they resisted the action of the atmosphere and did not react with the vehicle. The compounds had high specific gravity and refractive index, with the result that the pigments possessed great hiding power. Depending upon the base constituent employed, white or various colors were obtained. These alone, or mixed with extenders or other pigments, were used in connection with any vehicle ordinarily employed in the formulation of coating compositions. In a specific example, titanic acid obtained by the thermal hydrolysis of ilmenite solution, and containing some combined or adsorbed sulfuric acid, was mixed with an equivalent amount of slaked lime and heated at a temperature sufficiently high to effect the formation of crystalline calcium titanate, $CaTiO_3$. To bring about the combination of the sulfate radical present, an excess of the calcium compound was employed. The product obtained was of a white or

yellowish color and had a high hiding power and other excellent pigment properties. Such reactions were found to take place more readily in the presence of boric acid or borates.[28]

Alkaline earth titanates of pigment grade were prepared by heating hydrous titanic oxide, free of sulfuric acid, with the corresponding carbonate at 750° to 880° C. in the presence of an accelerator such as hydrochloric acid.[29] The residual sulfuric acid was removed from the pulp by washing, after treatment with sodium or ammonium acetate. In a specific operation, sulfuric acid-free hydrous titanic oxide representing 100 parts of the anhydrous material was dispersed in water and coagulated by adding 248 parts of barium carbonate to get an intimate mixture. The composite precipitate was treated with 3 parts hydrochloric acid and calcined at 840° C. to form barium titanate having porous particles.

To insure intimate mixing of the components, precipitated titanic hydroxide was dispersed in water with the aid of a halide of an alkaline earth metal, and an alkaline earth metal oxide, hydroxide, or carbonate was added to bring about coagulation.[30] The composite precipitate was separated from the liquor and calcined at 840° C. to produce the corresponding titanate. Titanium oxide obtained by the thermal hydrolysis of ilmenite solutions was mixed in stoichiometric proportions with barium or calcium carbonate and heated at 1100° C. to form the corresponding titanate.[31]

According to another method of manufacture, a mixture of titanium dioxide and an alkaline earth carbonate, hydroxide, or oxide was heated at 500° to 800° C. until the titanate was formed, and then at 800° to 1100° C. until the product showed sharp interference lines on an X-ray photograph.[32] Barium titanate showed tetragonal structure.[33] Calcium titanate of improved color and brightness was obtained by heating at 850° to 975° C. a mixture of titanium dioxide and calcium oxide containing 5 per cent magnesium oxide, 1 per cent silica, and 2 per cent antimony trioxide.[34]

A pigment consisting of calcium titanate and a solid solution of titanium dioxide in calcium titanate was produced by heating an intimate mixture of calcium carbonate and titanic oxide pulp, such as is obtained by the thermal hydrolysis of sulfate solutions.[35] Alkaline earth metal titanates suitable for direct use as pigments were conveniently prepared by reaction in the wet condition at relatively low temperatures of a mixture of hydrous titanic oxide and an alkaline earth metal hydroxide or carbonate.[36] The product was subsequently subjected to calcination (950° C.) to increase the

density and tinting strength and develop specific pigment properties. To illustrate, hydrous titanium oxide was washed free from sulfuric acid and slurried in water to a solids concentration of 15 per cent. An equimolecular amount of barium hydroxide was then added to the slurry, and the system was heated to boiling and maintained for 1 hour. Practically complete reaction took place, with the formation of a precipitate of barium titanate. The suspension was then filtered, and the product was dried and heated at a temperature of 950° C. for 1 hour. Calcination increased the density of the barium titanate from 5.43 to 5.94. In preparing some of the other titanates of the group, for example, calcium titanate, by this method, it was necessary to employ autoclave temperatures corresponding to a pressure of 60 pounds per square inch.

Pigments containing magnesium titanate (Mg_2TiO_4) [37] were prepared by heating an intimate mixture of titanium dioxide and magnesium oxide or hydroxide at 900° C. The latter component was present in any proportion up to that corresponding to the ortho-titanate, and extenders such as calcium and barium sulfates were added to form composite products. The reaction was accelerated by a small proportion of hydrochloric acid. Plunkett and Warner [38] prepared a product consisting primarily of magnesium titanate chemically combined with 3 to 12 per cent silica and alumina; the ratio of the silica to alumina varied from 8 to 1 to 12 to 1. Practically all the particles were within the range of 0.5 to 2 microns, and the effective index of refraction was 2.15.

A pigment consisting partly or wholly of zinc orthotitanate [39] was obtained by calcining a mixture of 1 mole titanic oxide with 2 moles zinc oxide at 800° C. Small proportions of potassium sulfate were added to the original mix to accelerate the reaction, and such extenders as barium sulfate and calcium sulfate were included in some compositions. According to a method developed by Monk, [40] hydrous zinc oxide was added to a titanium sulfate solution which was then heated to 80° C. to effect hydrolysis. The precipitate, after washing with water, was treated with magnesium oxide to neutralize the residual sulfuric acid, and the resulting magnesium sulfate was washed out. A small proportion of hydrochloric acid was added to the mixed pulp, with agitation, to form a small proportion of colloidal titanium oxide to act as catalyst, and the product was intimately mixed with an equimolecular amount of zinc oxide and calcined to produce the titanate. A similar pigment was prepared by heating a mixture of 0.9 to 2 moles of zinc oxide and 1 mole of titanium dioxide at 500° to 800° C. to effect complete

reaction, and this intermediate product was further heated to 1100° C.[41] Crystalline zinc magnesium titanate suitable for use as pigment was formed by calcining a mixture of the three oxides.[42]

Solid solutions of titanium dioxide in zinc orthotitanate were stabilized against decomposition at elevated temperatures by forming the product in the presence of a small proportion of a phosphate compound.[43] An equimolecular mixture of anatase titanium dioxide and zinc oxide was heated at 700° C. for 5 hours to form the orthotitanate. Two parts by weight of this product were mixed with 100 parts anatase titanium dioxide and 0.2 part phosphorus pentoxide, and the system was calcined at 900° C. for 3 hours. The reaction product consisted of anatase titanium dioxide and a solid solution mixture. An equivalent mixture, calcined without the phosphate compound, showed rutile; that is, the anatase was converted to rutile.

Double or compound titanate pigments,[44] characterized by high tinting strength and low reactivity with paint vehicles, were produced by calcining the corresponding oxides, hydroxides, or carbonates. Examples of such products are $2ZnO \cdot TiO_2$, $2CaO \cdot TiO_2$, and $2PbO \cdot TiO_2$.

Cobalt titanate [45] of pigment grade has been prepared by calcining an intimate mixture of hydrous titanium oxide and cobalt carbonate at 800° to 950° C. for several hours. The product obtained at the lower temperatures was yellowish, but with more severe calcination the color graded through green to bluish. Hydrolytically precipitated titanic oxide, which had been purified by neutralization and washing, gave best results. Titanates of nickel and manganese were prepared in a similar manner.

From thermal, microscopic, and X-ray studies, Grieve and White [46] constructed thermal equilibrium diagrams for the system manganous oxide-titanium dioxide and found that these components showed two compounds, manganous metatitanate, $MnO \cdot TiO_2$, and manganous orthotitanate, $2MnO \cdot TiO_2$.

Espenschied [47] prepared pigments consisting entirely or in part of lead metatitanate corresponding to the chemical formula $PbTiO_3$ by calcining a uniform mixture of hydrous titanium dioxide and a reactive lead compound such as the monoxide or basic carbonate in stages. The temperature was first held within a range just sufficient to effect the reaction, 600° C., and after the formation of lead titanate was complete it was raised to a value high enough to develop a crystalline structure, 850° C. Commercial hydrous titanium oxide, as obtained by the thermal hydrolysis of sulfate solutions,

contains a few per cent of closely held sulfuric acid, and if this product was used as a source material, a corresponding amount of lead sulfate was formed. Reaction of the primary constituents was found to take place only in equimolecular proportions, so that titanium dioxide in excess of this proportion appeared in the final product in the unreacted form.

In carrying out the process, a weight of washed and uncalcined hydrolysis product, containing 26 kg. of titanium dioxide and 2.1 kg. sulfuric acid, was treated with aqueous ammonia to reduce the acid to 6.55 per cent (based on solids), after which the ammonium sulfate formed was washed out. This partially neutralized hydrous oxide pulp was reslurried in water, 72 kg. of finely divided litharge was gradually added, and the whole mass was milled together for 1 hour to insure thorough mixing. The suspension was then dewatered, dried, and fed into a rotary calciner, the speed and temperature of which were so regulated that the reaction mixture traveled through a zone at a temperature of 500° to 750° C. in 2 hours, and through a second zone at 750° to 900° C. in 4 hours. The calcined product containing 94 per cent lead titanate, 5 per cent lead sulfate, and 1 per cent titanium dioxide was pulverized for use as pigment. It was a yellow or cream-colored crystalline solid having an effective specific gravity of 7.7 and an effective index of refraction of 2.8.

Pigments containing lead titanate were obtained by calcining mixtures of a lead oxide or basic carbonate with hydrous or dry titanium dioxide [48] at temperatures of 500° to 900° C. Barium sulfate or other extenders were added to produce composites. Such products, containing as low as 0.1 to 5 per cent lead titanate, possessed exceptionally good pigment properties, although higher proportions were also employed. Pure titanium dioxide, having its particles coated with lead titanate in quantities insufficient to have an appreciable influence on the color, brightness, or opacity, showed improved resistance to chalking and was reactive with paint vehicles. However, pigments with shades of color ranging from the white of titanium dioxide to the clear yellow of lead titanate were obtained by increasing the proportion of lead entering into combination from a relatively small amount up to that chemically equivalent to all the titanium component. Hydrous oxide of titanium, as precipitated commercially, contains a small amount of sulfuric acid; if this material is used, part of the lead may be converted to sulfate and appear as such in the final product. This residual acid may be neutralized, however, by treatment with an alkaline compound, sodium

hydroxide, and the resulting sulfate may be readily washed out with water.

A pigment of the composite type, containing lead titanate, was prepared by calcining a mechanical mixture of the extender, hydrous titanium oxide and lead monoxide. As an example, 100 kg. of titanium dioxide in the hydrous form was mixed intimately with 2.5 kg. of finely divided litharge and calcined at a temperature of 600° C. to effect reaction.

An intimate mixture of basic lead carbonate and hydrous titanic oxide suitable for conversion into lead titanate was obtained by co-precipitation from a solution of titanium and lead salts by addition of sodium carbonate.[49] The composite precipitate was filtered, washed, and calcined to bring about the reaction.

In a study [50] of the compound, a mixture of 1 mole titanium dioxide and 1.5 moles litharge was heated at 800° C. to effect combination. The excess lead oxide was extracted from the cooled reaction product with acetic acid, leaving lead titanate of pigment grade containing 25.5 per cent titanium dioxide and 73.5 per cent lead monoxide. It was not attacked by cold sulfuric acid or aqueous alkali, but it was decomposed by hot sulfuric acid, and partially decomposed in nitric and hydrochloric acids. It was not darkened by hydrogen sulfide.

A pigment somewhat similar to minium, with excellent antioxidant properties and reactive with drying oils, was prepared by calcining at 600° to 1000° C. a mixture of pulverized ilmenite with metallic lead or a compound such as the oxide, acetate, or basic carbonate.[51] The titanium content of the ore reacted to form lead titanate. In general the amount of lead employed was considerably less than that theoretically required to combine with all the titanium of the charge, but equivalent or greater proportions could be used. By regulating this ratio and by varying the conditions of calcination, a variety of colors was obtained. In a specific operation, 1000 kg. of pulverized ilmenite was intimately mixed with 50 kg. of litharge and calcined for 4 hours at 900° C. The product containing lead titanate was ground to produce a reddish-brown pigment.

The whiteness of impure titanium dioxide pigments may be improved by converting the iron present to ferrous titanate.[52] Such discolored material was heated at 850° to 1100° C. in an atmosphere of carbon monoxide to reduce all iron present to the ferrous state without affecting the titanium dioxide, after which the mixture was further heated to produce black ferrous titanate which increased the apparent brightness and covering power of the product. Such pig-

ments possessed a grayish cast instead of the original brownish tone caused by the ferric oxide.

A general method for producing titanate pigments was developed by Lederle, Gunther, and Brill.[53] Suitable compounds (oxides, carbonates, hydroxides) of base metals such as calcium, magnesium, zinc, lead, nickel, and cobalt were precipitated along with hydrous titanium oxide from aqueous media to get an intimate mixture. The composite product was filtered and washed, then heated, first at 500° to 800° C., until titanate formation was complete, and then up to 1100° C. to develop crystalline structure.

To illustrate, 1000 g. of finely divided calcined titanium dioxide was suspended in 10 liters of solution containing 1260 g. calcium chloride, and a sufficient amount of aqueous 20 per cent sodium carbonate was added to convert the calcium component to carbonate. The titanium dioxide settled out of suspension, along with the precipitated calcium carbonate, and the resulting finely divided and uniform mixture was washed free from impurities and filtered. It was then heated at 750° C. for 2.5 hours until the titanate formed. The temperature was then raised to 950° C. and held at this point for 1 hour to develop crystalline structure. After cooling the material was pulverized, mixed with water to form a free-flowing slurry, heated in a rotating autoclave for 2 hours at 200° C., and dried. The final product was calcium metatitanate of pigment grade, having a pure white color, a soft smooth texture, low oil absorption, and a uniform particle size. Alternatively, the starting mixture of titanium dioxide and calcium carbonate was subjected to a pressure treatment in the presence of water containing a trace of hydrochloric acid for 3 hours at 200° C. prior to calcination.

From a study of rates of reaction between various forms of titanium dioxide with calcium oxide and lead oxide, it was found that anatase was more reactive than rutile.[54] At 1000° to 1200° C., $CaO \cdot TiO_2$ was formed, and it was stable at lower and higher temperatures.[55] After continued heating at 1350° to 1400° C., $3CaO \cdot TiO_2$ was formed.

Chapter 17

CHLORIDE PROCESSES OF PIGMENT MANUFACTURE

Processes for the production of pigments from titanic chloride involve thermal hydrolysis of aqueous solutions or the high-temperature splitting (oxidation) of the anhydrous compound. Such solutions may be prepared directly by the action of hydrochloric acid on certain titanium minerals and secondary products, although the more available ores—ilmenite, arizonite, and rutile—are attacked very slowly, if at all, by this reagent, and they are usually treated with chlorine gas at elevated temperature. Anhydrous tetrachloride obtained in this manner is dissolved in water in a separate step to produce solutions of the desired composition.

The earliest investigators fused the ores with alkali metal compounds (sodium carbonate, potassium bisulfate) and dissolved the melt in dilute hydrochloric acid. Many titanates are soluble in hydrochloric acid, but such solutions would necessarily be impure. Similar products may be prepared indirectly by dissolving ortho-titanic acid at room temperature, or by adding an alkaline earth chloride to regular sulfate solutions. The resulting alkaline earth sulfate would be insoluble and could be readily removed by settling or filtration.

Hydrochloric Acid Attack

Llewellyn [1] reported a process for decomposing titanium ores with hydrochloric acid in which the ground ore (ilmenite) was digested with the aqueous acid at 50° to 60° C. for a long period of time. After cooling to room temperature, the liquor was filtered to remove any undissolved residue, and the solution containing titanic and iron chlorides was heated at 85° to 90° C. to precipitate the titanic acid. A relatively low temperature was employed during the digestion step to prevent loss of dissolved titanium by hydrolysis. Dissolution was accelerated by introducing gaseous hydrogen chloride continuously or intermittently into the system to maintain the optimum concentration as the reaction proceeded. [2] According to Riley, [3] the whole of the titanium content of titaniferous iron ores

may be dissolved in hydrochloric acid. Solutions containing 100 g. titanic chloride per liter were prepared by dissolving the residue from bauxite after the Bayer process.[4]

By heating finely divided silicate ores of the sphene class,[5] under controlled conditions with 10 to 20 per cent excess hydrochloric acid of concentration above 15 per cent, the titanium content was converted to chloride and held in solution during the entire extraction process. The acid-ore mixture was first heated under reflux at 40° to 50° C. to avoid loss of hydrogen chloride before the strength of the acid had been reduced by reaction, and to build up a concentration of titanic chloride sufficient to arrest hydrolysis as the temperature was later raised. Losses due to hydrolysis were further reduced by raising the temperature very slowly to the boiling point in 24 hours.

Ores containing iron in the ferric state, such as arizonite,[6] were first subjected, at 550° to 650° C., to the controlled action of a reducing gas to convert the ferric compounds to ferrous without the formation of metallic iron. The treated ore was then digested with dilute hydrochloric acid under a pressure corresponding to 135° to 180° C. to effect dissolution.

Vigoroux and Arrivant[7] prepared the tetrachloride by the action of hydrochloric acid gas on ferrotitanium. The alloy was heated to a low redness in a porcelain tube, and dry hydrogen chloride was passed through. Reaction proceeded, with the evolution of heat. The ferric chloride formed, condensed in the cooler part of the tube, and tended to clog the passage, while the titanium tetrachloride distilled over and condensed in a receiving vessel. According to a modified procedure, the iron content was selectively dissolved from the alloy with dilute hydrochloric acid, and the residue, containing 80 to 90 per cent titanium, was separated from the oxides and treated with the dry gas as before.

Sulfate solutions of titanium, such as are obtained from ilmenite by commercial methods, were converted to the chloride by treatment with an equivalent amount of calcium, barium, or strontium chloride.[8] The precipitate of insoluble alkaline earth sulfate was removed by filtration, leaving the solution of titanic chloride.

Chlorination

TITANIUM DIOXIDE. According to Pamfilov and Shtandel,[9] titanium dioxide chlorinated to the tetrachloride, but carbon should be present in the charge to take up the oxygen and prevent reversal

of the reaction. Up to 600° C. carbon dioxide was chiefly formed, but above this temperature the monoxide was the main product. Excess chlorine reacted with the carbon monoxide to form phosgene. Ferric oxide and calcium oxide, if present, reacted with titanium tetrachloride to give titanic oxide, ferric chloride, and calcium chloride. Silicates yielded some silicon tetrachloride.

Barton [10] heated a mixture of titanium dioxide and soft coal until the volatile constituents had been driven off, and treated the cinder with chlorine at 650° C. to form the tetrachloride. Similarly, a mixture of crude titanic oxide and carbon was heated with chlorine at 600° C., and the reaction products were led into an expansion chamber maintained at 136° C., where the ferric chloride condensed. The vapor of titanium tetrachloride was then passed through a filter plate, also at 136° C., to a condenser.[11] According to another modification, the tetrachloride was prepared by subjecting an ignited mixture of titanium dioxide and lampblack to the action of a stream of chlorine gas.[12] A porous product, which allowed free entry of chlorine,[13] was obtained by coking at a red heat a briquetted mixture of titanic oxide and sawdust or peat. Once initiated, the heat of reaction was sufficient to maintain the chlorination temperature. In the presence of wood charcoal the reaction went to completion at 500° C.[14] The action of chlorine sufficient to cause at least 1 per cent of the titanic oxide to react per hour started at 800° C.[15] By passing a mixture of carbon monoxide and chlorine over titanium dioxide at a rate of 1 liter per hour for 3.5 hours, 37.4 per cent of the charge was chlorinated at 600° C., and 80.7 per cent at 1050° C.[16] Thus an increase in temperature greatly increased the rate. Employing lampblack instead of carbon monoxide, 67 per cent of the titanium dioxide reacted in 1.5 hours at 600° C., and 79 per cent at 1050° C.

The equilibrium gas mixture,[17] formed on treating titanic oxide and carbon with chlorine at 400° to 1000° C., contained from 30 to 50 per cent by volume of titanium tetrachloride. The other gases were carbon monoxide and carbon dioxide, and as the temperature rose the proportion of monoxide increased at the expense of the dioxide.

In a pilot-plant study of chlorination of briquets, made by heating a mixture of 3 parts rutile, 1 part charcoal, and 1.75 parts thin tar binder, unground rutile was as effective as ground and more effective than titanium dioxide pigment.[18] The chlorine efficiency was 94 per cent with 70 per cent conversion of the charge, but decreased if all the charge was consumed. The condensed liquid, after separation

from ferric chloride by decantation, was clear and yellow, and contained 99 per cent titanium tetrachloride with 0.02 per cent iron. Redistillation from copper gave a colorless product.

The optimum temperature of chlorination of titanium dioxide-carbon mixtures was reported to be much lowered in the presence of manganese dioxide catalyst.[19] In an actual operation, the temperature at which the tetrachloride formed was reduced from 500° to 480° C. by including 0.2 per cent manganese dioxide in the charge. Titanomagnetite concentrates gave a high yield only above 600° C., and the process was complicated by the sublimation of ferric chloride. Sphene reacted rapidly only above 800° C. Titanic oxide was attacked faster than silica, but slower than calcium oxide.

Most of the iron of ilmenite or titaniferous iron ores was selectively dissolved by leaching with hydrochloric acid, leaving a residue of crude titanic oxide. Such a product, obtained by digesting the finely ground ore with hot hydrochloric acid in a closed vessel, was elutriated from heavy sand, mixed with soft coal, and heated in a stream of chlorine gas at 600° to 700° C. to produce the tetrachloride,[20] which, after purification by fractional distillation, was dissolved in water, and the solution was subjected to thermal hydrolysis. The precipitate was washed and calcined to yield titanium dioxide of pigment grade, while the liquor containing the liberated hydrochloric acid was employed to leach the iron from another batch of ilmenite.

ILMENITE. Titanium tetrachloride was formed by subjecting a briquetted mixture of ilmenite and coal to the action of chlorine at a temperature sufficient to volatilize the compounds formed, but not above 750° C.[21] The products were purified by redistillation. Donaldson[22] heated ilmenite or similar ores with charcoal at a temperature below 1000° C., but sufficiently high to reduce all iron compounds to the metallic state without much reduction of titanium. The iron was selectively converted to ferric chloride and volatilized by the action of chlorine at a temperature between 350° and 1000° C. and the residue of titanium dioxide was chlorinated according to normal procedure. A tough granular mass having very desirable form for chlorination was obtained by drying a mixture of 20 to 25 parts powdered coke with 50 to 60 parts ilmenite and 20 parts titania in colloid suspension.[23] The suspension was prepared by agitating 100 parts of sulfuric acid-free hydrous titanic oxide (40 per cent solids) with 15 parts of concentrated hydrochloric acid. Briquettes formed by heating a mixture of titanium ore, ground to 0.5

mm., and coal, with a starch paste as binder, out of contact with air proved quite satisfactory.[24]

In a study [25] of chlorination of titanomagnetite concentrate containing 44 per cent titanium dioxide, 31.4 per cent ferrous oxide, 16.9 per cent ferric oxide, 1.84 per cent silica, 0.05 per cent chromium oxide, 0.72 per cent manganous oxide, 0.6 per cent copper, 2.76 per cent magnesium oxide, 0.15 per cent phosphorus pentoxide, and 0.16 per cent water, at temperatures up to 600° to 650° C., in a porcelain tube in the presence of solid carbon with a gas velocity of 3 liters per hour for 6 hours, a yield of 98 per cent was obtained. The concentrate was treated in the powdered form and in briquettes of various sizes. Optimum temperature of chlorination of titanium dioxide in the presence of manganese dioxide was found to be 450° to 480° C., and above 500° C. without the catalyst, with a yield of about 90 per cent.

Separation of iron from ilmenite or similar ore was effected by subjecting the finely ground material, (300 mesh) without previous reduction, to selective chlorination in the absence of a reducing agent, at 800° C.[26] At this temperature the iron only was attacked, and the resulting ferric chloride was removed from the reaction chamber by sublimation as formed, leaving a residue of titanium dioxide together with a small amount of silica and other impurities. Chlorination of the titanium component began at 815° C., and this temperature should not be exceeded during the initial stage of the process. Best results were obtained above 800° C. The ferric chloride was deposited in cooling chambers and later decomposed by heat to regenerate chlorine for use in treating more ore. Residual titaniferous material was chlorinated in another operation, or it was used directly or was purified by conventional methods.

The amount of iron and titanium recovered as volatile chlorides from ilmenite was effectively controlled by regulating the amount of reducing agent in the charge during chlorination, and with a carbon content within an optimum range, the major portion of the iron was removed without appreciably attacking the titanium.[27] If a proportion of carbon in excess of the optimum was employed, some titanium was volatilized as the tetrachloride, and with ore mixtures containing large excesses of the reducing agent the major portions of both iron and titanium were converted to chlorides and removed from the reaction chamber by volatilization. Within the temperature range of 700° to 1150° C., changes in the temperature did not require significant changes in the carbon concentration, but below this range a slight increase in the proportion was necessary to produce

best results. The optimum carbon concentration may be greatly changed, however, by mixing oxidizing gases, e.g., air and oxygen, with the chlorine. Most efficient results were obtained by chlorination above 500° C., but, in general, excessively high temperatures caused sintering of the ore and prevented proper distribution of the gases. Although reaction took place below 500° C., the rate was very slow and the heat developed was not sufficient to maintain the operating temperature. A working range of 700° to 1150° C. gave most efficient chlorination, as well as maximum iron removal with minimum losses of titanium. In a series of tests, samples were prepared by mixing various proportions of finely ground ore and carbon with 12 per cent molasses (based on the ore), and the compositions were formed into briquettes ⅛ inch in diameter and baked at 400° C. to remove volatile hydrocarbons. These were then chlorinated at a uniform rate of 140 liters of gas per minute per kilogram of sample for 5 minutes at 980° C., employing chlorine-air mixtures of different compositions. With no added carbon other than that derived from the molasses, and employing chlorine with no admixed air, 79 per cent of the iron initially present in the ore was removed. A similar briquetted mixture containing 4 per cent added carbon, under the same chlorination conditions, resulted in removal of 97.5 per cent of the iron with a loss of only 3.4 per cent of titanium, while treatment in the presence of 6 per cent carbon resulted in the removal of 99 per cent of the iron and 22 per cent of the titanium.

The absolute and relative amounts of iron and titanium removed were changed considerably if a mixture of equal volumes of chlorine and air was used as the chlorinating agent. Thus, with 4 per cent carbon in the charge, 85 per cent of the iron was removed without significant loss of titanium, while at a carbon concentration of 8 per cent, approximately 95 per cent of the iron and only 5 per cent of the titanium were converted to chlorides. Employing a gas mixture of 20 per cent chlorine and 80 per cent air, and briquettes containing 8 per cent added carbon, 84 per cent of the iron and practically no titanium were reacted, while 13 per cent carbon resulted in removal of 95 per cent of the iron and only 5 per cent of the titanium. Ordinarily the temperature was maintained by regulating the rate of introduction of ore, carbon, chlorine, and air, but the reaction could be cooled, if desired, by introducing a diluent gas such as carbon dioxide or nitrogen.

According to a typical operation of the process, 100 parts ilmenite ore containing 26 per cent iron and 35 per cent titanium was mixed with 7 parts of carbon and 12 parts of molasses, and the composition

was formed into briquettes having an average size of ⅛ inch in diameter and baked at 400° C. Total carbon after baking was 7.6 per cent. Ten parts by weight of the briquetted mixture was heated to 980° C., and a stream of 5 parts by weight of chlorine and 1 part by weight of air was passed through the charge maintained at the initial temperature. The residue contained 93.2 per cent titanium dioxide and 0.74 per cent ferric oxide. This corresponded to a removal of 99 per cent of the original iron with a loss of only 4 per cent of the titanium.

In general, the most desirable and most economical bonding agents for forming briquettes of this type were petroleum asphalt, natural asphaltum, tar, pitch, sulfite liquor from paper making, and bituminous emulsions.

By a very similar process [28] employing chlorine without admixed air, a uniform mixture of 100 parts ilmenite ore containing 26 per cent iron and 35 per cent titanium, mixed with 6 parts of coal and 12 parts of molasses, was made up into briquets having an average size of ½ inch and baked at 400° C. to remove volatile hydrocarbons. The final product contained 7.2 per cent carbon. Ten parts by weight of the briquetted mixture was heated to 815° C., and 20 parts chlorine was passed through the charge in a continuous stream. Temperature of the system was maintained at 815° C. The unreacted residue, containing 90 per cent titanium dioxide and 0.71 per cent ferric oxide, was chlorinated to yield a relatively pure titanium tetrachloride. Removal of iron from the original ore was 98 per cent complete, while the loss of titanium was only 4 per cent. After initiating the reaction, the briquetted ore and chlorine were introduced into the reaction chamber, together with a gaseous reducing agent, at such a rate that the temperature was maintained above 600° C. without adding air or a solid reducing agent other than that employed as a binder for the titanium-bearing material.[29] To prevent the upper part of the bed from cooling to cause condensation of vaporized ferric chloride, Cleveland[30] preheated the titanium material and regulated the rate of charging.

From another approach, ilmenite, chlorine, and a gaseous reducing agent, natural gas, were introduced into a reaction chamber at such a rate that the heat evolved by the chlorination maintained the temperature above 600° C.[31] At this temperature the iron and titanium chlorides were volatilized as formed.

In chlorinating ores at elevated temperatures, heat may be conveyed from the chlorination residue to fresh starting materials by a stream of gas which does not enter into the reaction.[32]

SPHENE. A sphene concentrate containing 25.42 per cent titanium dioxide, 26.82 per cent silica, 28.45 per cent calcium oxide, 2.98 per cent ferric oxide, 1.32 per cent ferrous oxide, 1.29 per cent magnesium oxide, 0.13 per cent manganous oxide, 7.18 per cent phosphorus pentoxide, and 0.14 per cent water was chlorinated at temperatures between 290° and 900° C., although best results were obtained at 800° to 900° C.[33] In general, the chlorination of sphene was found to be much more difficult than of titanomagnetite. The chlorine distribution among the components of the concentrate was not favorable. Calcium chloride was formed rapidly, although the final recovery of titanium was almost complete.

CARBIDES. According to Oreshkin,[34] chlorine combined with titanium carbide faster and at a lower temperature than with a mechanical mixture of titanium dioxide and carbon. The former reaction took place at 200° C. Carbide prepared by fusing an ore, such as rutile or ilmenite, with coke in an electric furnace gave good yields on chlorination at an incipient red heat.[35] The crude titanium tetrachloride produced was freed from vanadium by shaking with sodium amalgam and from chlorine by distillation. The slag (soluble with difficulty) formed in the hearth of aluminum furnaces employing titaniferous bauxite contained, in addition to coal and lime, 45 to 47 per cent titanium as carbide and was readily attacked by chlorine at 400° to 500° C.[36] The titanium tetrachloride formed was separated from chlorides of iron and aluminum by distillation and converted to the sulfate by heating with sulfuric acid at 160° to 200° C. Hydrolysis of aqueous solutions of the sulfate salt by boiling for 7 hours gave a recovery of 96 per cent. Brallier[37] prepared the tetrachloride by passing chlorine over the carbonitride, containing 70 to 75 per cent titanium, in a furnace consisting of a steel shell lined with carbon slabs and cooled by a water spray.

In a commercial method of manufacture the ore or concentrate, usually rutile, was first heated with coke in an electric furnace to form the carbide or cyanonitride, and this product was treated with gaseous chlorine at elevated temperatures.

ALLOYS. Favre[38] chlorinated alloys of titanium, iron, and copper, containing from 0.1 to 20 per cent of the latter element, and reported that the reaction began at 250° C. Such products were obtained by subjecting a mixture of a copper-magnesium-aluminum alloy and ilmenite to cupro-aluminothermic treatment, or by subjecting a mixture of copper and ilmenite to electrosilicothermy. A mixture of titanic and ferric chlorides was obtained by passing dry chlo-

rine over powdered ferrotitanium at a dull red heat.[39] Industrial alloys containing up to 55 per cent titanium were employed. Titanium tetrachloride, being the more volatile, distilled past the ferric chloride in the reaction tube and condensed in a water-cooled worm. The product was colored red by ferric chloride, but because of its low solubility the greater part of this impurity was removed by filtration. Further purification by fractional distillation gave a colorless liquid which did not fume on exposure to air. According to a related method, most of the iron was dissolved from the alloy by treatment with dilute hydrochloric acid, and the residue, containing 80 to 90 per cent titanium, was chlorinated as in the previous operation. De Carli [40] treated an iron-titanium alloy with chlorine at 400° to 500° C. and purified the product by fractionation after allowing it to stand over mercury or copper.

The brittle mass obtained by plunging ilmenite, heated to 1000° C., into cold water, was pulverized, mixed with half its weight of aluminum powder, heated to 500° C., and the reaction was set off by a layer of dry titanium dioxide and aluminum, which was ignited by a magnesium flame. This reduced reaction product [41] was placed in a combustion tube and heated to redness in a current of chlorine. Ferric chloride deposited in the cooler portion of the tube, while the titanic chloride was carried on to the condensing chamber and was purified by distillation. The first fraction contained some silicon tetrachloride and chlorine.

Helbig [42] mixed titanium dioxide in gel form with powdered carbon and a small amount of the oxide of a metal of the sixth or seventh group of the Periodic System, dried the product, and treated it with chlorine at a red heat. Once initiated, the reaction proceeded exothermically.

In the absence of carbon, the approximate decreasing order of reactivity of chlorine at 1000° C. was reported to be iron oxide, magnesium oxide, calcium oxide, titanium dioxide, zirconium oxide, alumina, and silica.[43] More complex compounds containing these oxides, silicates, and spinel were less reactive. Furthermore, the rate of reaction depended upon the thermal history and was less for strongly calcined materials.

CONTINUOUS CHLORINATION. Ilmenite or similar raw materials were chlorinated in a continuous process [44] by introducing the ore, carbon, and chlorine into a reaction chamber at such a rate that sufficient heat was evolved by the reaction to maintain the temperature above 600° C. Maximum efficiency was obtained, however, at 850°

to 1250° C. For most purposes better results were obtained by holding the carbon content at 15 to 35 per cent of the ore. Proportions below this range were insufficient to insure complete chlorination of both iron and titanium components, while on the other hand excessive amounts made temperature control difficult. A quantity of briquets 0.25 to 0.75 inch in diameter was prepared from a mixture of 100 parts ore, 23 parts coke, and 14 parts molasses, and baked at 600° C. to drive off the volatile materials. These carbonized pellets were introduced at a rate of 120 pounds an hour into a furnace having a 15-inch internal diameter and preheated to 1000° C. Chlorine was introduced at the rate of 2 to 2.5 pounds per minute, and the temperature was maintained at 850° to 1000° C. throughout the run without externally heating the furnace. Vapors were withdrawn from the furnace as formed, and cooled to 40° C., with the result that 85 per cent of the ferric chloride and 25 per cent of the titanium tetrachloride condensed in this operation. The condensed chlorides were transferred to another part of the receiver, and the titanium tetrachloride was revolatilized by passing exhaust gases of the furnace over the mixture. Agnew and Cole [45] fed the briquetted material into the reaction chamber upon a movable framework base, and introduced chlorine above the frame and air below. Movement of the framework removed unchanged material and gangue from the reaction zone, which was maintained at approximately 600° C. To effect continuous chlorination of titanium dioxide in the presence of coke, Brallier [46] kept the temperature up to the required 700° C. by causing titanium carbide or cyanonitride to react simultaneously. According to another modification, the necessary heat for the reaction was supplied by introducing silicon into the reaction zone. [47] The silicon tetrachloride formed was separated by fractional distillation.

In a cyclic process, [48] selective chlorination of ilmenite or titaniferous iron ore was carried out in two steps at different temperatures to effect a separation of iron and titanium chlorides. Finely ground ore was mixed with powdered coal or charcoal and formed into briquets with the aid of a fatty or tarry bonding material, such as oil, tar, or pitch, and subjected to a reduction roast in a furnace or rotary kiln which also served for the chlorination vessel. The briquetted material was heated, in the absence of air, at 800° C. for 1 to 2 hours in a retort which was sealed, except for a small opening to allow escape of the gases driven off, and then cooled in the reducing atmosphere to 350° C. At this stage dry chlorine gas was passed through the reduced mass, and at this temperature iron only

was attacked and the ferric chloride formed passed over in the vapor form and was condensed in a cooling chamber. The direction of flow of chlorine was then reversed, and the temperature was raised to 550° to 600° C. Within this range the titanium component was attacked and the resulting tetrachloride, containing traces of chlorides of iron, silicon, and vanadium, passed into a cooling tower where it was condensed. The crude material was purified by redistillation.

However, by mixing a reducing gas with the chlorine, the two operations were carried out simultaneously and the ore was chlorinated directly without incorporation of coal or the formation of briquettes. Chlorides of iron, silicon, and titanium were formed successively as the temperature was increased, and these were separated by fractional distillation. After purification the titanium tetrachloride was dissolved in cold water, and the solution was neutralized with an alkali or alkaline earth metal base. The precipitate of orthotitanic acid was filtered, washed, and redissolved in strong sulfuric acid, and this sulfate solution was hydrolyzed by boiling to obtain a good yield of titanium dioxide of high purity. Slight hydrogenation, brought about by introducing the purified gas or by addition of metallic zinc to the liquor, facilitated the precipitation. The product was filtered, washed, and calcined for pigment use, and the filtrate, consisting primarily of dilute sulfuric acid, was concentrated for use in dissolving more gelatinous oxide.

By another approach the purified titanium tetrachloride was dissolved directly in dilute sulfuric acid, and the hydrogen chloride liberated was passed into a solution of sodium hydroxide. The titanium sulfate solution obtained was subjected to thermal hydrolysis, as before. In either case the alkali metal (sodium) chloride liquor was electrolyzed to recover chlorine and the corresponding hydroxide, both of which were again used in the process. The ferric chloride was dissolved in water and reduced in solution to the ferrous salt by boiling with ferrous sulfide, according to the reaction, $2 FeCl_3 + FeS \rightarrow 3 FeCl_2 + S$. Sulfur was separated by filtration, and the solution was electrolyzed to recover chlorine for reuse and metallic iron as a by-product. Agnew [49] treated the effluent from the electrolytic cells with lime to precipitate the remaining iron as hydroxide, and used the separated hydroxide to neutralize more liquor prior to electrolysis so that the cyclic process resulted in no loss of iron.

As a vaporized mixture of chlorides of iron and titanium obtained from ilmenite was cooled, the ferric chloride condensed first, but

some of the solid remained suspended in the tetrachloride vapor and was carried over into other parts of the condenser system where it tended to clog the apparatus. This troublesome suspended material was removed from the vapors by spraying with cooled liquid titanium tetrachloride.[50] After removal of the iron component, the titanium tetrachloride was condensed to the liquid state. The initial condensation could be controlled to produce the required amount of liquid titanium tetrachloride to wash the suspended ferric chloride from the uncondensed vapors.[51] Following this procedure the purified tetrachloride vapor was condensed to the liquid state without clogging the apparatus. By a similar process, the vaporized mixture was washed first with cold liquid titanium tetrachloride to remove the suspended ferric chloride and then with water to condense the tetrachloride and at the same time form an aqueous solution for hydrolysis.[52]

AGENTS OTHER THAN CHLORINE. Chloroform[53] reacted with hot powdered titanium dioxide to form the tetrachloride, carbon monoxide, and hydrochloric acid. According to Chauvenet,[54] the chlorinating power of phosgene was inferior to that of a mixture of chlorine and carbon, because of the endothermic nature of the decomposition of carbonyl chloride.

Jenness[55] heated a gaseous mixture of chlorine and di- or higher chlorides of sulfur to near the boiling point of the sulfur compound, and passed the mixed vapors over heated ores to form titanium chloride and sulfur. Similarly, on heating rutile with sulfur monochloride, the iron and vanadium components were first attacked and distilled off as chlorides, leaving almost pure titanium dioxide.[56] The latter could be converted slowly to the tetrachloride, but the mixture was difficult to purify, since the titanium compound had about the same boiling point as sulfur monochloride.

Before chlorination, the titanium-bearing silt obtained as a waste product in purifying bauxite was treated with hydrogen sulfide to convert the iron component to the nonreactive sulfide.[57] Sulfur chloride, chlorine, or carbon tetrachloride was used successfully as the chlorinating agent.

By passing the mixed vapors, obtained by chlorinating clays or similar materials in the presence of coal, into a fused mass of equimolecular amounts of aluminum chloride and alkali metal chloride containing suspended solid alkali metal chloride, the iron and aluminum fractions were removed, leaving the silicon and titanium tetrachlorides.[58]

Purification of Titanium Tetrachloride

As already noted, the crude tetrachloride prepared by the chlorination of titaniferous materials usually contains free chlorine, together with small proportions of dissolved compounds of iron, silicon, vanadium, and other elements derived from the charge, and is of a yellowish or reddish color. This discoloration has been ascribed to vanadium oxychloride, ferric chloride, and uncombined chlorine. Since ferric chloride is only slightly soluble in the product, the greater part of it may be recovered, along with other suspended particles, by filtration after cooling to room temperature. The other constituents, with the exception of vanadium, may be readily separated by fractional distillation, and this impurity may be removed by a similar operation after treating the liquid with sodium amalgam [59] with gold, silver, mercury, copper, or bronze; [60] or with iron or carbon.

The vanadium in crude titanium tetrachloride is probably present as the oxychloride or tetrachloride, both of which are volatile liquids at ordinary temperature and cannot be recovered by ordinary distillation. Jenness and Annis [61] found that the addition of small amounts (0.25 to 0.50 per cent) of certain organic materials to the crude tetrachloride caused the formation of vanadium compounds which were insoluble and nonvolatile at temperatures considerably above the boiling point of the titanium tetrachloride. These complex compounds were separated by distillation or by such mechanical methods as filtering or centrifuging. Effective organic compounds polymerized in the crude tetrachloride product and reacted with the vanadium during polymerization to form nonvolatile, readily separable compounds.

Examples of this type of compounds are rubber, crude or vulcanized, balata, art gum, polymerized sulfonated oil, soy-bean oil, cottonseed stearin, Russian mineral oil, and acetylene gas. Ordinary rubber was partly polymerized, but further polymerization took place, producing a black, brittle, granular solid. The resulting compound with vanadium was separated from the liquid by distillation, filtration, or centrifuging. Russian mineral oil contained a large proportion of naphthenate compounds which were the active agents. It also appeared that titanium tetrachloride was a good polymerizing agent. The action during polymerization appeared to consist first of forming an addition compound with the crude liquor, followed by a reaction between this and the vanadium, with the liberation of titanium tetrachloride and the formation of a finely polymerized prod-

uct. The polymer contained two atomic proportions of chlorine to each of vanadium.

The extent of removal was dependent upon time, temperature of the reaction, and the per cent of agent employed. For instance, 0.10 per cent balata did not remove the vanadium after refluxing for 1 hour, but under the same conditions 0.25 per cent effected complete removal. Also, 0.5 per cent balata produced vanadium-free tetrachloride after only 15 minutes refluxing at 136° C., but contact with this proportion of agent at 20° C. for 16 hours did not effect complete removal. Vanadium was recovered quantitatively from the polymerization product.

According to Pechukas,[62] crude titanium tetrachloride was purified and decolorized by treatment with carbon having absorptive or adsorptive properties, followed by distillation. Best results were obtained by using carbon black, such as lampblack, bone black, and gas black, although charcoal and petroleum coke were also found to be effective. The carbon containing the absorbed or adsorbed impurities or their reaction products was recovered and regenerated for further use. Dependent upon the initial color of the liquid and the proportion of carbon used, the time and temperature of the operation were capable of considerable variation. If the discoloration was secured by liquid contact, refluxing at atmospheric pressure (136° C.) for a period of time in excess of 10 minutes, followed by distillation, was found to give a yield of purified titanium tetrachloride above 99 per cent. In treating the vapors, any convenient temperature above the boiling point of the liquid proved satisfactory.

In an example, 100 parts of crude yellow titanium tetrachloride was agitated with 4.1 parts lampblack and heated under a reflux condenser at 136° C. for 15 minutes, after which the treated liquor was distilled rapidly to yield a colorless liquid.

According to Gage,[63] crude titanium tetrachloride was purified by distillation after treatment with lower chlorides of titanium. These compounds could be formed in place by reducing a portion of the original compound, as for instance with hydrogen. In an actual operation, 100 parts of crude yellow titanium tetrachloride was treated with 5 parts of the trichloride, heated under a reflux condenser at 135° C. for 2 hours, and then distilled rapidly in an atmosphere of dry carbon dioxide. The condensate was a clear, colorless liquid. Metallic impurities, such as compounds of iron, vanadium, and manganese, were precipitated from the crude material by treatment with an active sulfide, such as hydrogen sulfide or arsenic sulfide,[64] or by passing hydrogen sulfide into the liquid in

the presence of 0.05 to 0.5 per cent ferric stearate or other heavy metal soap.[65] A process developed by Meyers,[66] effective in removal of vanadium compounds, consisted of mixing an alkali metal soap with the tetrachloride, followed by evaporation. No heating was required. From 0.1 to 1.0 per cent of a sodium or potassium soap of stearic, myristic, palmitic, oleic, or lauric acid gave best results, and the vanadium content was reduced below 0.001 per cent. Meister [67] added 5 to 10 g. crystalline ferrous sulfate per liter to crude titanium tetrachloride, refluxed for 1 to 6 hours, and distilled to get a product of high purity. Purification was similarly effected by a simple distillation after refluxing with small quantities of alkali metal hydroxide, powdered iron, tin, antimony, or copper and water.[68] In an example, 4 g. to 10 g. sodium hydroxide, 1 g. to 5 g. water, and 3 g. to 20 g. zinc powder were added to 1 liter of crude tetrachloride, the mixture was refluxed for 2 to 4 hours at atmospheric pressure, and distilled to get a colorless product containing less than 0.001 per cent vanadium. At the same time iron was reduced to less than 0.001 per cent, calculated as ferric oxide. From another approach, the vaporized material was heated at 800° to 1000° C. in the presence of hydrogen to reduce the impurities to solid compounds which were readily separated.[69]

Stoddard and Pietz [70] purified titanium tetrachloride in a pilot plant by distillation with copper. One and one half per cent copper was the minimum amount that produced a colorless product. The powder used was prepared by reducing finely ground cuprous oxide with hydrogen. In a specific test, a colorless product was obtained by distillation after heating the crude tetrachloride with 1.5 per cent copper powder at 98.5° C. for 15 minutes. Oleic acid also gives good results, but it offers several disadvantages.

Hydration or Dissolution of the Tetrachloride

In dissolving anhydrous titanium tetrachloride in water, an initial turbidity usually occurs as a result of the separation of oxychlorides or hydrous oxides. These compounds can be redissolved, however, if additional amounts of the anhydrous tetrachloride are added. Investigations revealed that the original precipitates were caused by the great rise in temperature that accompanies hydration. If no cooling was provided, the temperature of the solvent rose to above 100° C., until a concentration corresponding to 130 g. titanium dioxide and 250 g. hydrochloric acid was reached. At this point hydrochloric acid gas was evolved, and precipitation began to be

apparent. If more tetrachloride was added, the temperature decreased and the suspended material gradually dissolved to give a clear concentrated solution. The decrease in temperature in the second stage of the process occurred because the heat of evaporation of the hydrogen chloride was greater than the heat of solution of the titanium tetrachloride.

Because of losses of hydrogen chloride, the clear solutions obtained by this method contained tetravalent titanium and chlorine in an atomic ratio less than the theoretical 1 to 4, and usually about 1 to 2.7. Concentrations corresponding to 550 g. titanium dioxide and 600 g. hydrochloric acid per liter were readily attained.

Better results were obtained by employing dilute hydrochloric acid instead of water as the initial solvent.[71] Hydrogen chloride started boiling off at a lower temperature; the rise in temperature was less; and the degree of precipitation was decreased. Clear solutions of any practical concentration were obtained by mixing the anhydrous material in a similar manner with dilute aqueous titanium tetrachloride containing more than 150 g. free and combined hydrochloric acid per liter.[72] Dissolution in this manner was accompanied by a small increase in temperature and copious evolution of hydrogen chloride so that the final product contained a lower proportion of chlorine than that corresponding to the chemical formula $TiCl_4$. The working solvent was prepared by dissolving titanium oxychloride in an excess of concentrated hydrochloric acid and adjusting the product to a concentration corresponding to 60 g. titanium dioxide and 160 g. hydrochloric acid per liter. Once in operation, a portion of the clear concentrated solution was diluted with water and used as the initial solvent.

The process was carried out in a continuous manner by running the anhydrous tetrachloride and aqueous solvent simultaneously into a dilute titanic chloride solution containing more than 150 g. hydrochloric acid per liter. A typical product contained the equivalent of 550 g. titanium dioxide and 600 g. hydrochloric acid per liter, which corresponded to an atomic ratio of titanium to chlorine of 1 to 2.6.

Following these methods of preparing solutions of titanium tetrachloride, local overheating occurred, caused by the high heat of solution, with the result that some of the compound was lost by volatilization. This loss was reduced by vigorous agitation of the system and by cooling, but it could not be entirely avoided by these precautions. However, if the anhydrous material was introduced below the surface of the aqueous solvent, with constant agitation, losses resulting from evaporation were almost entirely avoided.[73]

One or more submerged pipes were employed for the anhydrous material; by passing a current of dry air or inert gas along with the tetrachloride, backing up in the pipes was prevented and danger of clogging by the basic precipitates was minimized. Water, hydrochloric acid, or dilute solution of the tetrachloride served as suitable solvents in the process.

Dissolution was also carried out in a continuous manner by simultaneously introducing the anhydrous material and the aqueous solvent through submerged feed pipes into a small initial quantity of the solution from a previous run. Concentration of the titanium chloride was adjusted by regulating the rate of addition of the two components. The product was removed continuously through an overflow outlet in the vessel.

Precipitation of Titanium Dioxide

Three general methods of obtaining titanium dioxide from titanic chloride have been employed: (1) hydrolysis of aqueous solutions by heating, by dilution, or by addition of alkali; (2) by introducing anhydrous titanium tetrachloride in the vapor phase, along with steam, into a reaction chamber; (3) by heating the anhydrous material in the vapor phase, admixed with air or oxygen at a high temperature, either indirectly or in a direct flame.

HYDROLYSIS OF SOLUTIONS BY BOILING. Titanium dioxide may be obtained commercially from the tetrachloride by hydrolytic precipitation effected by heating its aqueous solution or by bringing the anhydrous material in the vapor phase into contact with steam in a reaction chamber. By regulating the conditions and employing a suitable seeding agent, titanium dioxide of pigment grade can be produced. In large-scale operation, the splitting operation has the advantage that chlorine is recovered directly rather than hydrochloric acid. Before use, however, the tetrachloride must be carefully purified, a step not so important in the methods involving hydrolysis of aqueous solutions, since most of the objectionable impurities remain dissolved in the acid hydrolysis liquor.

Thermal hydrolysis of chloride solutions in the presence of nuclear titanic acid, precipitated from a separate portion of the solution by moderate heating after reduction of the acidity to a pH of between 2 and 3 either by dilution or by neutralization with an alkali, yielded a product which on calcination gave a pigment of the rutile type having a correspondingly high tinting strength.[74] Such seeding compounds obtained at low acidity, for instance a pH of 5 to 7, had

little nucleating power. On the other hand similar products obtained from very acid solutions, for example those having a hydrogen ion concentration greater than pH 2, were very active, but stabilization required particular care. Very active nuclei were found to be less stable at high temperatures and were cooled quickly to preserve their effectiveness. To obtain the maximum degree of stability, the seed was subjected to a controlled cooling at a rate dependent upon the original acidity, and the temperature was maintained during the precipitation.

As a rule, a proportion of nucleating compound from 5 to 8 per cent of the titanium dioxide to be precipitated was required, and it was not essential that the seed dissolved in the main hydrolysis solution. Nuclei less active than normal were employed in larger proportions, and for the same results concentrated solutions required more seeding agent than dilute solutions. Freshly prepared titanic chloride solutions were more reactive than older ones and thus required less nucleation.

Titanium prepared in accordance with this process was of the rutile crystal form, and the resulting pigments had higher tinting strengths than the anatase products obtained from sulfate solutions.

In a typical operation, a chloride solution containing the equivalent of 150 g. titanium dioxide per liter and having an atomic ratio of titanium to chlorine of about 1 to 3 was employed for hydrolysis and for preparation of nuclei. A portion of the solution was treated with aqueous sodium hydroxide to bring the pH to 2.5, heated at 80° C. for 30 minutes to develop the nucleating property, and cooled quickly to below 50° C. The solid product precipitated in this manner was the active seeding agent and was usually separated and washed before use, although the original suspension in the mother liquor was effective. A quantity of the seeding material containing 7 g. titanium dioxide was added to each liter of the original chloride solution and the mixture was heated at 100° C. Hydrolysis proceeded rapidly and was complete in 10 minutes. The precipitate of hydrous titanic oxide was washed, treated with 2 per cent potassium bisulfate, heated slowly to 900° to 950° C. in a rotary calciner, and held at this temperature for 15 minutes.

According to another approach, anhydrous titanium tetrachloride, free from iron, copper, and vanadium, was allowed to run into 18 per cent hydrochloric acid, and the resulting oxychloride was dissolved in water to produce a solution containing the equivalent of 320 g. titanium dioxide and 353 g. hydrochloric acid per liter. Dilute aqueous sodium hydroxide at 40° C. was added to a portion

of the solution, with agitation, and during the procedure the temperature rose to 60° C. The amount and concentration of the reagents were so chosen that after mixing the pH of the solution was 2 and the strength corresponded to 30 g. titanium dioxide per liter. This liquor was then heated to 80° C., held at this temperature for 30 minutes, and cooled to below 60° C. by adding cold water in such proportion as to bring the concentration to 20 g. titanium dioxide equivalent per liter.

The remainder of the original solution was then mixed with concentrated hydrochloric acid to yield a liquor in which the atomic ratio of titanium to chlorine was 1 to 4, and seed was added to supply titanium dioxide equal to 8 per cent of that to be precipitated. After dilution with water to 55 g. titanium dioxide and 100 g. hydrochloric acid per liter, expressed as hydrolysis products, the liquor was heated to 90° C. in 12 minutes and held at this temperature for 30 minutes to effect hydrolysis. The washed precipitate was reslurried in water to 250 g. per liter solids, treated with potassium bisulfate in an amount equal to 1.5 per cent of the titanium dioxide, dewatered, and calcined at 950° C. for 30 minutes. Both pigments were of the rutile crystal modification, and after milling and pulverizing by the conventional methods exhibited tinting strengths one fourth to one third higher than the best anatase products.

Similarly, titanium tetrachloride seeded with a sol prepared by heat-treating a diluted portion of the same solution gave a hydrolysis product which, after calcination at moderate temperature, exhibited the rutile crystal structure and the high tinting strength corresponding to this modification of titanium dioxide of pigment grade.[75] Heat treatment developed the nucleating property of the sol, and both temperature and time were important, since overcuring lessened the effectiveness of the product. Longer periods of heating at lower temperatures were required to develop the maximum nucleating efficiency. Best results were obtained by curing solutions, containing the equivalent of 10 to 20 g. titanium dioxide per liter, at 80° to 90° C. for 10 to 15 minutes. The resulting sol presented a slight opalescence, and the particles could not be separated by the conventional methods of filtration and washing. However, the degree of dispersion of the colloidal titanic oxide and its homogeneity did not seem to have a great influence on the nucleating property of the sol.

Tetrachloride solutions for hydrolysis contained the equivalent of 140 g. to 160 g. titanium dioxide per liter, and the proportion

of nuclei was from 5 to 9 per cent of the total titanium dioxide. Solutions of high purity gave products of higher opacity and better pigment properties, although the presence of iron and organic impurities was not found to be detrimental to efficient nucleating properties of the sol. Any ferric iron was reduced to the ferrous state to prevent its precipitation with the titanium.

To illustrate, 1 liter of an aqueous solution of titanic chloride, containing the equivalent of 15 g. of the dioxide, was transferred to a flask fitted with a mechanical stirrer and a reflux condenser, and heated to 80° to 85° C. After 10 minutes at this temperature, 1250 ml. of an untreated solution at room temperature was added, containing the equivalent of 150 g. titanium dioxide per liter, and the' mixture was heated to boiling and refluxed for ½ hour. The precipitate was filtered, washed, calcined, and pulverized to yield a pigment of the rutile crystal form having a tinting strength 20 to 25 per cent higher than the conventional anatase product along with excellent color and brightness.

Barksdale and Plechner [76] prepared very effective nuclei by heat-treating dilute solutions of titanium tetrachloride to which an alkaline agent had been added to convert from 10 to 60 per cent of the potential or active hydrochloric acid to a salt that would not hydrolyze under the conditions subsequently employed. The efficiency of the nucleating composition, and the quality of the pigment obtained, were found to depend upon a number of co-related factors which may be more conveniently described separately.

The solutions employed were prepared by diluting commercial titanium tetrachloride with water; because of losses of hydrochloric acid gas by volatilization, the proportion of chloride was usually less than that corresponding to the chemical formula $TiCl_4$, and in some solutions was as much as 10 to 15 per cent. However, the method was also applicable to solutions produced indirectly, as by dissolving orthotitanic acid in hydrochloric acid or by adding alkaline earth metal chlorides to solutions of titanium sulfate. Iron and other polyvalent heavy metals, present as impurities, were reduced to the more stable toward hydrolysis, lower valent form, by electrolytic means or by adding zinc, scrap iron, or sulfurous acid. Concentrations expressed as hydrolysis products, according to commercial practice, between 250 g. and 400 g. per liter titanium dioxide and 450 g. to 640 g. per liter hydrochloric acid, gave best results, and at the same time permitted more economical operation of the process. Such solutions were used for hydrolysis and for preparation of the seeding agent.

In preparing nuclei, an alkaline compound was added to a portion of the original solution in such proportions that from 10 to 60 per cent of the potential hydrochloric acid, normally from 30 to 45 per cent, was neutralized. The composition of the alkali used was of minor importance provided that it formed a compound nonhydrolyzable under the conditions of processing, and such bases as calcium hydroxide, potassium carbonate, sodium hydroxide, aqueous ammonia, sodium sulfide, and certain organic amines fulfilled this requirement to a high degree. It is evident that the chlorides of these agents were soluble in water and that they dissolved in the solution. Calcium oxide, in addition to its low cost, gave optimum results but since it was relatively insoluble in water, it was added in the form of a slurry or in the solid state.

Concentration of nuclear solutions from 5 g. to 30 g. per liter titanium dioxide proved effective, but best results were obtained within the range of 10 g. to 20 g. per liter. Obviously the potential hydrochloric acid was less than that corresponding to the normal salt.

Proper curing of the nuclei was a function of both temperature and time of heating, and could be followed roughly by the degree of turbidity developed, which reached a translucent stage. In general, 10 minutes at 80° to 90° C. developed the nucleating property to the maximum degree, although the same results were obtained by holding the system at a lower temperature for a longer period of time, for instance at 70° to 75° C. for 1 hour. The exact change in the solution was not established, but a large part of the titanium component was converted from the crystalloidal to the colloidal condition. Partial neutralization did not render the solution of titanic chloride more susceptible to precipitation during the subsequent heat treatment, as might be expected, but on the contrary made it more stable. Such a solution, after treatment with the alkali, could be heated for a longer period of time at a given temperature without precipitation of titanic oxide. However, with both solutions precipitation would finally occur, but curing was not carried to this stage. The greatest efficiency of the nuclear composition, as measured by the properties of the pigment obtained, was found to be the combined effect of the partial neutralization and the heat treatment.

In carrying out the hydrolysis step, the manner of mixing the components was not particularly important, but for convenience the nuclear composition was usually added to the solution of titanium chloride to be precipitated. The nuclei were employed at the temperature formed or cooled to room temperature, and the hydrolysis solution could be preheated to the evolution of hydrogen chloride

gas. Titanium, supplied to the hydrolysis mixture by the seeding composition of from 1 to 10 per cent of the total, exerted satisfactory nucleating properties, but from 4 to 6 per cent yielded titanium dioxide of the best pigment properties.

The efficiency of the nucleation and the quality of the resulting products were influenced by the final concentration of the hydrolysis mixture, and values from 125 g. to 150 g. per liter titanium dioxide proved most satisfactory. After mixing the nuclear suspension with the chloride solution water was added, if necessary, to adjust the concentration to the desired value. If the hydrochloric acid content exceeded 225 g. per liter, hydrogen chloride gas was evolved on boiling, and arrangement for its recovery or disposal was provided. The seeded mixture was heated to boiling and maintained to bring about the hydrolytic reaction. A yield of 97 per cent or better was usually obtained after ½ hour, in some tests in 15 minutes, and rarely was it necessary to continue the boil for 1 hour.

In an actual operation, a solution prepared by diluting commercial titanium tetrachloride with water and containing 340 g. per liter of the dioxide and 545 g. per liter hydrochloric acid (expressed as hydrolysis products), was employed. To a portion of this solution containing the equivalent of 15 g. titanium dioxide was added 7 g. hydrated lime (the equivalent of approximately 1 mole of hydrochloric acid per mole of titanium tetrachloride), with stirring. This partially neutralized clear solution was diluted with water to 1 liter, heated to 85° C. in 20 minutes, held at this temperature for 10 minutes, with agitation, and cooled rapidly to room temperature. The product was an opalescent colloidal solution of titanium dioxide. This composition was added rapidly to 1000 ml. of the original solution, with constant agitation, and 500 ml. water was introduced to adjust the final concentration to 144 g. per liter titanium dioxide. The seeded mixture was heated from room temperature to boiling in 30 minutes, and refluxed for 1 hour to precipitate 97 per cent of the titanium as hydrous oxide. This product was filtered, washed with water acidified with sulfuric acid to prevent peptization, and calcined at 800° C. for 1 hour to produce a pigment of the rutile crystal form having excellent brightness and color and the very high tinting strength of 1750 by the Reynolds method.

A nucleating composition, prepared by heating a titanium tetrachloride solution containing the equivalent of 5 g. to 30 g. of the dioxide per liter and 0.5 to 2.0 mole proportions of a nonoxidizing univalent anion such as chloride, acetate, or formate, at 80° to 90° C. for 10 to 15 minutes to develop a decided opalescence, accelerated

and directed the thermal hydrolysis of relatively concentrated aqueous solutions of the tetrachloride.[77] The cation had no appreciable influence upon the hydrolysis, but only colorless compounds, for example, calcium chloride, sodium metaborate, and potassium acetate, were of practical value. Approximately 5 per cent of the nuclear suspension, based on the titanium content, was required, and the hydrolysis product after calcination at a relatively low temperature was of the rutile crystal modification and had the correspondingly high hiding power and brightness. Von Bichowsky[78] prepared a solid nucleating agent corresponding to the formula $Ti(OH)_3Cl \cdot 5H_2O$ by evaporating a solution of titanium hydroxy chloride. The product was effective in the hydrolysis of chloride and nitrate solutions.

To produce titanium tetrachloride solutions more amenable to directed hydrolysis on addition of external nucleating agents, the initial solution was subjected to heat treatment at a temperature below that at which titanium dioxide would be precipitated, and the residual colloidal material was coagulated and separated.[79] This heat treatment removed residual components which would have a nucleating influence.

Hydrolysis is effected without introducing externally prepared nuclei by adding concentrated titanium tetrachloride solution to hot water and boiling the resulting mixture to complete precipitation of the titanium dioxide.[80] The solution is added to the water at a sufficiently slow rate to insure the initial formation of colloidal titanium dioxide particles which serve as seed for the product formed later in the process. In general, the concentration of the chloride solution and ratio of solution to water are such that, after hydrolysis, the resulting liquor has a composition corresponding to constant boiling hydrochloric acid. Yields of 96 per cent are obtained in $\frac{1}{2}$ hour, and the washed and calcined product gives a rutile pigment of excellent covering power and brightness. In an example, 1000 ml. of a titanium tetrachloride solution containing 300 g. of titanium dioxide and 480 g. of hydrochloric acid, expressed as hydrolysis products, was added in 5 minutes to 1000 ml. of boiling water, with constant agitation. The mixture was heated to boiling in 15 minutes and refluxed for 30 minutes to effect hydrolytic precipitation of the titanium. This precipitate was filtered, washed, and calcined, without further treatment, at 850° C. to produce a pigment of the rutile crystal form possessing excellent brightness and color and having a tinting strength one third higher than that of the commercial anatase products. A similar process employs more dilute solutions.[81]

Readily filterable hydrous titanic oxide of high purity was obtained by the thermal hydrolysis of aqueous solutions of the tetrachloride containing not more than 0.1 mole of polyvalent negative coagulating ion derived from oxalic, tartaric, phosphoric, or citric acids or their alkali metal salts per mole of titanium dioxide.[82] Alternatively, the same results were obtained by adding the tetrachloride solution to hot water containing the coagulating ions. The mixture was boiled to complete the precipitation of the titanium. Since hydrous titanic acid was readily peptized in dilute aqueous hydrochloric acid, better results were obtained by employing very dilute sulfuric acid as the washing liquor.

According to a specific operation of the process, anhydrous titanium tetrachloride was dissolved in water to obtain a solution containing the equivalent of 15 per cent titanium dioxide. All iron present was reduced to the ferrous condition. To prevent reoxidation during processing, about 2 g. per liter of titanous ions was formed. One thousand pounds of this solution was added in 1 hour to 7000 pounds of boiling water containing 2 pounds of citric acid, and by the end of the mixing operation 95 per cent of the titanium had precipitated as hydrous oxide in a coagulated form that was easily filtered and washed. The washed pulp was calcined at 700° to 1000° C. to produce a rutile pigment of good color and high tinting strength. By employing specially purified raw materials, titanium dioxide pure enough for a standard in volumetric analysis was obtained by this method.[83] A precipitate of high quality was obtained by hydrolytic decomposition of aqueous titanium tetrachloride in the presence of 25 to 30 per cent sodium sulfate.[84] At 69° to 72° C., 10 per cent solutions gave highest yields and 5 per cent solutions the poorest, although at 98° to 101° C. there was no difference in recovery from solutions containing from 5 to 20 per cent titanium tetrachloride.

Darling[85] obtained finely divided titanium dioxide by passing the tetrachloride, in vapor form, into a boiling solution of glucose. During the process, glucose was converted to glutaric acid. Jenness[86] added the tetrachloride to a solution of hydrochloric acid to form a mixture of basic chlorides in the form of a dry yellow granular powder, and separated and calcined the product to obtain fluffy white titanium dioxide of pigment grade.

Processes for the manufacture of titanium dioxide pigments from siliceous minerals of the sphene class were reported by Alessandroni.[87] If the finely ground ore was heated with hydrochloric acid of concentration above 15 per cent, the titanium values were dis-

solved and held in solution during the extraction step, along with calcium compounds and minor constituents of the ore such as iron, magnesium, aluminum, and vanadium, leaving a residue composed essentially of silica. However, to hasten dissolution of the soluble constituents, and to obtain a maximum recovery of titanium, an excess of 10 to 20 per cent hydrochloric acid was employed. The mixture was heated under reflux at 40° to 50° C. for several hours to avoid loss of hydrogen chloride before the strength of the acid had been reduced by reaction, and to build up a concentration of titanic chloride sufficient to prevent hydrolysis at the higher temperatures employed in the later stages. During the next 24 hours the temperature was raised gradually to the boiling point, and heating was continued until no more titanium dissolved. Since compounds of polyvalent elements such as iron were more readily attacked by the acid and were more stable toward hydrolysis in the lower valent condition, the reaction was carried out in the presence of 1 to 2 per cent of a reducing agent such as titanous chloride or stannous chloride. Iron, for example, was reduced before the titanium, and the added agent was not sufficient to reduce an appreciable amount of the tetravalent titanium. The final solution, containing most of the titanium of the original ore as chloride along with nonhydrolyzable chlorides of calcium, magnesium, ferrous iron, aluminum, and other metals, and some free hydrochloric acid, was cooled and separated from the siliceous residue by decantation or filtration. It was then concentrated to the desired strength by vacuum evaporation and subjected to thermal hydrolysis to precipitate the titanium as hydrous oxide. By leaving the silica suspended in the original solution, composite pigments were produced.

In an example, 1000 pounds of finely ground sphene (100 to 200 mesh), analyzing 32 per cent titanium dioxide, 29.6 per cent silica, 18.7 per cent calcium oxide, 12.9 per cent alumina, 1.43 per cent ferrous oxide, 4.29 per cent ferric oxide, 1.12 per cent magnesia, and 0.10 per cent manganese oxide, was mixed with 8300 pounds of 29.5 per cent hydrochloric acid in a vessel fitted with a reflux condenser and held initially at 40° C. for 4 hours to avoid loss of hydrogen chloride. During the next 24 hours, as the acid concentration was reduced by reaction, the temperature was raised gradually to the boiling point, about 107° C. At this stage the reaction had practically ceased and the mixture was cooled and filtered. Ninety-four per cent of the titanium was recovered in the filtrate, which weighed 9100 pounds and contained 300 pounds titanic oxide equivalent, 1420 pounds free hydrochloric acid, and 369 pounds calcium chloride.

This solution was next subjected to the usual reducing treatment, concentrated in a vacuum evaporator at 50° C. to 11 per cent titanium dioxide, and poured into three volumes of boiling water containing an amount of oxalic acid equal to 0.05 per cent of the titanium dioxide to be precipitated. The liquor was heated to its boiling point in a tank provided with an outlet for the recovery of hydrochloric acid, and held at this temperature until 95 per cent of the titanium was precipitated as hydrous oxide. The hydrolysis product was filtered, washed, calcined, and pulverized to produce a practically pure titanium dioxide pigment of the rutile crystal form possessing excellent color and brightness and high tinting strength.

In a cyclical process, ilmenite ore was extracted with hydrochloric acid to leave a titanium dioxide concentrate which was chlorinated to form the tetrachloride.[88] The titanium tetrachloride was dissolved in water and hydrolyzed by boiling to precipitate the dioxide. Hydrochloric acid liquor formed during hydrolysis was used to extract more ilmenite ore. Leach liquor from the first step was electrolyzed to yield iron and chlorine, and the chlorine was used to form more titanium tetrachloride.

Dutt[89] prepared titanium dioxide from solutions obtained by dissolving the residue from bauxite, after the Bayer process, in hydrochloric acid. Such solutions contained up to 100 g. per liter titanic chloride; any considerable excess of hydrochloric acid was neutralized and the iron component was reduced to the ferrous state. Sodium acetate was added in an amount equal to one tenth of the titanium tetrachloride present, and the liquor was boiled to precipitate hydrous titanic oxide. After almost complete neutralization, the filtrate was treated with barium salts to precipitate barium vanadate.

Barton[90] treated a sulfuric acid solution of ilmenite with barium chloride, filtered off the insoluble barium sulfate formed, and heated the resulting chloride solution at 100° C. for 5 to 8 hours to effect hydrolysis. The precipitate of hydrous titanic oxide was washed, dried, and calcined to produce a product of 98.2 to 99.8 per cent purity. By an opposite approach,[91] the clear solution obtained by dissolving 1 volume of titanium tetrachloride in 2 volumes of water was mixed with 0.35 volume of 95 per cent sulfuric acid and heated to distill off the hydrogen chloride. Heating was continued until fumes of sulfur trioxide were given off. During this period the temperature rose to 150° C., and most of the hydrochloric acid was recovered. The residue, consisting of a white friable mass that contained 77 to 80 per cent titanic oxide, 18 to 20 per cent sulfur trioxide, and 2 to 3 per cent chlorine, was transferred to a calcining

furnace and heated to expel the remaining acids, leaving relatively pure, friable titanium dioxide of chalky appearance having a specific gravity of 3.65. Paint films pigmented with this material had a bluish cast, apparently because of its amorphous nature and very fine particle size.

A solution of titanium hydroxide in 2 molecular proportions of hydrochloric acid was boiled with sulfuric acid in the presence of kieselguhr and aluminum silicate to effect hydrolysis.[92] Similarly, aqueous titanium tetrachloride was neutralized to precipitate a gelatinous oxide, and this product was washed and redissolved in 25 per cent sulfuric acid. The solution was boiled to bring about hydrolytic reaction. Precipitation was facilitated by slight hydrogenation, which was accomplished by direct introduction of the gas or by addition of zinc.[93] The amorphous oxide was calcined to produce a crystalline pigment.

Gelatinous titanic oxide of exceptional purity was obtained by treating aqueous titanium tetrachloride with an alkali metal carbonate.[94] On boiling in a bath slightly acidified with sulfuric acid, the precipitate passed into a dense unctuous mass of pigment grade. Hydrous oxide, prepared by heating dilute tetrachloride solutions in air, acted as a strong protective colloid.[95]

The reactions of chloride solutions of titanium were carried out in an iron vessel surrounded by a casing through which water flowed.[96]

According to Atanasiu,[97] the rate of hydrolysis of titanic chloride solutions increased with temperature and dilution, and platinum exerted a catalytic action. The reaction was bimolecular, indicating a series of consecutive reactions between the colloidal and aqueous phases. Alcohol diminished the rate. Such solutions yielded hydrolysis products which gave rutile directly on calcination.[98] If precipitation was carried out in the presence of sulfate or phosphate ions, however, products were obtained which on moderate calcination showed the crystal structure of anatase but were transformed at higher temperatures into rutile.

VAPOR PHASE HYDROLYSIS WITH STEAM. Very finely divided, soft, and uniform titanium dioxide of pigment grade was obtained by the hydrolytic reaction between vaporized anhydrous titanium tetrachloride and steam or water vapor at temperatures of 300° to 400° C.[99] The vapor phases were heated separately to the required temperature before being introduced into the reaction chamber to prevent undesirable low-temperature reactions. For example, two

saturation vessels, constructed and operated after the fashion of an ordinary wash bottle, were employed to produce the vapors. One was charged with titanium tetrachloride and held at 120° C.; the other was charged with water and heated to 80° C. Air was passed through to produce two gaseous streams consisting of air and titanium tetrachloride, and air and steam in the volume ratio of approximately 1 to 1. The two gaseous mixtures were preheated separately to 400° C., and introduced simultaneously into an upright cylindrical reaction vessel heated externally to 400° C., in such proportions that for each liter of reaction space 1 liter per minute of the steam and air mixture (0.5 liter steam) and 0.1 liter of the tetrachloride-air mixture (0.05 liter titanium tetrachloride vapor) entered. The vapors were directed so as to transverse the reaction vessel in a downward direction, where they reacted to form titanium dioxide and hydrogen chloride, and the products passed into a dust chamber heated at 200° to 400° C. to prevent condensation or adsorption of the hydrochloric acid on the titania during the precipitation. Hydrochloric acid vapors emerging from the dust chamber were condensed and reused.

Even at decomposition temperatures as low as 300° C. titanium dioxide, practically free from chlorides, was obtained in almost quantitative yield, while the material separated at 380° to 400° C. possessed covering power equal to pigments produced from sulfate solutions calcined at 900° C. By this method a product suitable for direct use as pigment was obtained without the necessity of a calcination step.

According to a related process, vapors of titanium tetrachloride and water were injected into a closed collector maintained at an elevated temperature to effect hydrolysis, and the products of reaction were discharged tangentially to produce a forced circulating action within the chamber.[100] The titanic oxide was collected on a porous diaphragm while the hydrochloric acid gas and air passed through the openings.

A homogeneous finely divided titanium dioxide was obtained by the action of steam on titanium tetrachloride in admixture with a solid, inert, water-soluble salt, such as an alkali metal chloride or sulfate, at an elevated temperature.[101] One hundred parts titanium tetrachloride was mixed with 200 parts finely ground potassium sulfate to form a plastic mass which was heated to 300° to 400° C., and a current of steam was passed over the mix for 1 hour. Steam was then shut off, the temperature was raised to 800° C. and maintained for 15 to 30 minutes. The mass was cooled to room tempera-

ture, leached with water to remove the potassium sulfate, and the residue of titanium dioxide was further washed, dried, and pulverized for pigment use.

Thermal Splitting

In general, the reaction between titanium tetrachloride vapor and steam produces coarsely crystalline dioxide not well suited for pigment purposes. Furthermore, it is extremely difficult to provide apparatus that can resist the action of moist hydrochloric acid at the high temperatures employed. These difficulties were overcome, however, and a soft finely divided titanium dioxide of excellent pigment properties was produced from vaporized tetrachloride by a process in which the splitting reaction was brought about by oxygen or air at temperatures above 1000° C.[1,2] In carrying out the process, a saturation vessel, constructed and operated on the lines of a wash bottle, was charged with titanium tetrachloride and heated at 120° C. Nitrogen was passed through to produce a gaseous product consisting of approximately equal parts of the two constituents, and this mixture was passed simultaneously with preheated air into an upright cylindrical reaction tube heated by external means to 1100° C. The proportions and quantities of the agents were so regulated that for each liter of reaction space there was introduced, per minute, 1000 ml. of the tetrachloride-nitrogen mixture (500 ml. titanium tetrachloride vapor) and 1000 ml. air. In passing through the reaction vessel in a downward direction, the gases reacted to form titanium dioxide and chlorine, and the products were discharged into a dust chamber where separation was brought about. Titanium dioxide produced in this manner possessed excellent pigmentary properties and did not require subsequent processing.

To minimize coarsening and undesirable crystallization of the particles during the splitting reaction, the gaseous mixture of tetrachloride and air was raised rapidly to the reaction temperature. The gases were preheated, but to minimize premature reaction they were not mixed before reaching the splitting chamber, which was already heated to the required temperature. The choice of splitting temperature above 1000° C., and the gas velocity, could be regulated within wide limits.

This process had the advantage over the various types of hydrolytic decomposition in that the chloride component was recovered not as hydrochloric acid but as elemental chlorine gas which was used directly for attacking more ilmenite or other titanium raw material.

Finely divided titanium dioxide was obtained by bringing vapors

of the tetrachloride into the direct flame of a combustible gas or vapor.[103] For example, purified coal gas was loaded with titanic chloride vapors and ignited in air. Highly dispersed titanium dioxide resulted, and owing to its high specific volume it was carried along with the gas currents and separated in a chamber provided with several filtering materials or in precipitators of the Cottrell type.

By subjecting vaporized titanium tetrachloride to thermal decomposition in the presence of oxygen, titanium dioxide of pigment grade was produced without the formation of large crystals by keeping the vapors out of contact with hot surfaces within the chamber during the splitting reaction.[104] Apparently titanic oxide formed adjacent to the hot walls of the reaction vessel, deposited on the surface, and served as seed which grew to form large crystal agglomerates, and these reduced the average tinting strength of the product.

In carrying out this improved process, oxygen and titanium tetrachloride vapor, in the proportion of 3.3 moles of the former to 1 mole of the latter, were introduced continuously into a reaction chamber of sufficient size to permit thermal decomposition of the tetrachloride but to prevent a significant proportion from reaching the walls of the chamber. The reactants were preheated separately to the reaction temperature of 1500° to 1800° F. before bringing them together in the splitting chamber, where a temperature of 1500° to 1800° F. was also maintained. The collected titanium dioxide, in powder form, was further calcined to remove the last traces of chlorine. Pechukas and Atkinson[105] employed a special calcination chamber to heat titanium tetrachloride vapor with oxygen at 400° to 800° C. to produce a pigment of improved properties. Schornstein[106] introduced parallel streams of the vaporized tetrachloride diluted with an inert gas, and of air mixed with 2 to 70 per cent water vapor based on the oxygen component, both preheated at 800° to 900° C., into a chamber so that an oxidation reaction took place out of contact with the walls. In a similar process, titanic chloride and air were preheated separately to 1000° to 1100° C. and passed into a reaction chamber maintained at 750° C. by means of a cooling jacket.[107] The proportion of chloride to oxygen was 1 to 4. During the reaction a yellow-green flame burned at the outlet of the preheating tube and a pigment smoke issued from the other side of the reaction vessel. The pigment was very voluminous and possessed excellent whiteness.

To minimize crystal growth and produce titanium dioxide of pigment grade, the chloride vapor was not allowed to come into contact with hot surfaces of the reaction chamber. This was effected by

maintaining an atmosphere of nitrogen around the tetrachloride inlet.[108] A temperature of 1000° C. was employed. The same result was attained by causing the titanium tetrachloride vapor to react with an oxygen countercurrent in a vertical cylindrical furnace, and withdrawing the evolved chlorine so that it surrounded the area of introduction (inlet) of the tetrachloride.[109] This procedure prevented reaction from taking place at the hot surfaces.

A modified pigment was prepared by passing a hot vaporized stream of titanium tetrachloride over a metallic oxide to form a chloride of the metal and disperse it in the vapors.[110] The mixed chlorides were then decomposed in a suitable chamber by reaction with oxygen at high temperature. After filtering from the gas stream, the mixed oxides were further purified by calcination to remove the last trace of chlorine.

Chapter 18

FLUORIDE, NITRATE, SULFIDE, AND CHLORO-ACETATE PROCESSES OF PIGMENT MANUFACTURE

Fluoride Processes

Processes for the production of titanium dioxide based on fluoride solutions are different from those based on sulfates, chlorides, and nitrates. Chloride compounds are quite stable and, unlike the chlorides, nitrates, and sulfates, do not hydrolyze in solution on dilution or heating, so the titanium component is precipitated by adding ammonium hydroxide or other alkali after carefully purifying the solution to remove the heavy metal compounds, particularly those of iron, which would otherwise be thrown down as hydroxides along with the titanium component and so injure the color and other properties of the pigment. Considerable interest has been shown in this process, and it has been reported to offer promise. Certainly on a laboratory scale fluoride solutions yield pigments of excellent properties.

For removing silica from oxide compounds of titanium and vanadium and from clays the crude materials were treated with nonaqueous ammonium fluoride in a proportion less than that corresponding to the fluosilicate to produce a volatile compound ($SiF_4 \cdot 2NH_3$) which was distilled off.[1] By a related process, materials containing alumina, silica, titanium oxide, and vanadium oxide were transformed into complex mixtures of fluosilicates and fluorides by the action of fluorine or ammonium bifluoride.[2] The fluosilicates of ammonium, vanadium, and titanium were driven off by heating, leaving a residue of aluminum and potassium fluorides which were converted into chlorides by treatment with gaseous hydrochloric acid and ammonia. Titaniferous material containing siliceous impurities was treated with calcium fluoride and sulfuric acid at temperatures below 140° C. to form fluorides of all base constituents except the titanium.[3] These compounds were then removed by washing with acidified water. Silica and

titania were removed from bauxites or ores of chromium and manganese by heating with hydrofluoric acid or a mixture of fluorite and sulfuric acid to form the corresponding fluorides, followed by distillation,[4] leaving the other constituents in the residue.

Doremus [5] treated ilmenite with 20 per cent hydrofluoric acid and heated the mix with live steam to initiate and maintain the reaction. The product was dissolved in water and after separation of the insoluble residue an oxidizing agent such as hydrogen peroxide was added to the solution to convert all the iron to the ferric state, and potassium hydroxide was then added to precipitate potassium fluotitanate, fluozirconate, and fluosilicate. Of these, only the fluotitanate was soluble, and it was separated from the other constituents by leaching the mass with hot water. Titanium hydroxide, precipitated from the solution by adding ammonium hydroxide, sodium carbonate, or potassium hydroxide, was filtered, washed, and calcined. Hydrofluoric acid was recovered from the residue. The ferric fluoride solution from the first operation was treated with calcium chloride to obtain insoluble calcium fluoride and ferric chloride, or with potassium hydroxide to form ferric oxide and potassium fluoride. In the latter procedure the potassium fluoride solution was treated with lime to form calcium fluoride and potassium hydroxide.

According to a method developed by Svendsen,[6] the titanium component was separated from ores by volatilization as fluorides, dissolved in water, and precipitated as hydrous oxide of pigment grade by adding an aqueous alkali. On heating titanic oxide compounds with hydrofluoric acid or ammonium fluoride, a titanium-fluorine compound was formed, and this product at higher temperatures evolved titanium tetrafluoride or diaminotetrafluoride, depending upon the agent used in the treatment. However, a nonvolatile titanium oxyfluoride compound formed to some extent. If sodium-titanium sulfate was heated with a metallic fluoride, double decomposition took place, yielding titanium tetrafluoride and metallic sulfate. The normal titanium sulfate is unstable if it exists at all, and for this reason the stable double sulfate with an alkali metal or ammonium was used. Employing the ammonium double sulfate, a sufficient amount of the fluoride compound was added to prevent the formation of ammonium bisulfate, which would lead to the formation of oxyfluoride compounds. Metallic fluorides gave best results, since hydrofluoric acid and ammonium fluoride caused the formation of sulfuric acid or ammonium sulfate. The double sulfates were produced by heating titanium-oxygen compounds with

a mixture of ammonium sulfate and alkali metal sulfate, either normal or acid. Reaction took place above 280° C., but to prevent reduction by ammonia the temperature was held below 350° C., although toward the end of the operation it was raised to 400° C. The ammonium double sulfate was similarly produced by employing ammonium sulfate alone. Since ferrous iron produced troublesome ammonium sulfite, the ore (ilmenite) was roasted before the sulfate treatment.

Vaporization of titanium tetrafluoride took place about the same temperature at which the double sulfate was formed, but a higher temperature could be used, provided that it was held below the dissociation point of ferric sulfate. The tetrafluoride vapors evolved condensed, and at room temperature solidified to a colorless mass. Unlike silicon tetrafluoride it was soluble in water without hydrolysis, but the hydroxide was thrown down by aqueous ammonia. The precipitate obtained from dilute solutions in this manner had colloidal properties, although dense, readily filtered products were obtained by increasing the density of the original liquors either by increasing the concentration of titanium tetrafluoride or by adding a neutral salt other than titanium, such as ammonium fluoride. Similar results were obtained by dissolving ammonium fluoride in the ammonical liquor used in the precipitation.

The titanium tetrafluoride vapors were contacted directly with the ammonium hydroxide solution to precipitate titania, or they were first liquefied or solidified and then treated. By mixing the ammonia gas from the sulfate reaction with the titanium tetrafluoride vapors, titanium diaminotetrafluoride was formed.

As an example, calcined and pulverized titanium dioxide was mixed with 2 moles of ammonium sulfate and 1 mole of sodium sulfate for each mole of titanium dioxide, and heated in a rotating or muffle type of furnace at 300° to 350° C. to form sodium titanium sulfate. The escaping ammonia and water vapors were collected and used later in the operation. After reaction had ceased, sodium fluoride was added in the proportion of 4 molecular parts to 1 part of titanic oxide; the temperature was raised to 350° to 400° C. and held within this range until the evolution of fluoride vapors ceased. During the process the temperature did not exceed 400° C.

The furnace residue, consisting primarily of sodium sulfate, was used to regenerate the sodium fluoride and the sodium and ammonium sulfates used in these reactions. The titanium tetrafluoride vapors, together with the ammoniacal vapors first evolved, were

contacted with an aqueous ammoniacal solution of ammonium fluoride in a scrubber tower constructed of acid-proof stone or non-corrosive alloy (18 per cent chromium and 8 per cent nickel stainless steel). A temperature below 34° C. was maintained to prevent dissociation of normal ammonium fluoride into the bifluoride and ammonia, and by carrying out the reaction at even lower temperature denser precipitates were obtained. A considerable excess of circulating liquor was used. The product obtained from the scrubber, consisting of a suspension of hydrous titanium oxide in ammonium fluoride solution, was filtered, and the cake was washed, dried, and calcined to produce pigment.

A part of the filtrate, containing approximately the same amount of fluorine as that used in the reaction to vaporize the titanium, was used to regenerate sodium fluoride and ammonium sulfate, and the remainder was recirculated through the scrubber. The ammonium fluoride solution withdrawn was mixed with the sodium sulfate of the furnace residue to precipitate sodium fluoride, while sodium and ammonium sulfates remained in solution and were recovered by evaporation. After once establishing the cyclic process it was necessary to supply new reagents only to replace small mechanical losses.

If silica was present in the ore in a form that could be attacked by the fluoride, it would be volatilized along with the titanium, but the water liberated by the silicon fluoride caused the formation of oxyfluoride compounds of titanium. For this reason the silicon was removed before distillation of the titanium tetrafluoride, and this was accomplished during the sulfate formation by addition of calcium sulfate. Important reactions involved in the process are the following:

(1) $TiO_2 + Na_2SO_4 + 2(NH_4)_2SO_4 \rightarrow Na_2Ti(SO_4)_3 + 4NH_3 + 2H_2O$
(2) $Na_2Ti(SO_4)_3 + 4NaF \rightarrow TiF_4 + 3Na_2SO_4$
(3) $TiF_4 + 4NH_4OH \rightarrow Ti(OH)_4 + 4NH_4F$
(4) $4NH_4F + 3Na_2SO_4 \rightarrow 4NaF + 2(NH_4)_2SO_4 + Na_2SO_4$

Similarly, the titanium content of ores may be separated from other metallic constituents by distillation, after conversion into a complex volatile fluoride.[7] Silica, if present, is also converted to a volatile fluoride, but this compound may be readily separated since it is a gas at ordinary temperatures, while titanium tetrafluoride boils at about 290° C. Furthermore, the vaporization temperatures of the diaminotetrafluorides of silicon and of titanium are about 100° C. apart. Also, silicon tetrafluoride and its amino

compound are decomposed by water, and the silica is completely precipitated by the addition of a stoichiometrically equivalent amount of ammonia, while the corresponding titanium compounds dissolve in water without hydrolysis and the titania is precipitated only by addition of ammonia.

In operation, the ore is subjected to the action of a reactive fluoride compound (ammonium fluoride) under conditions so regulated as to produce a volatile titanium-fluorine complex. Such a compound, formed by gradually adding an excess of ammonium fluoride to the titanium oxide compound at a temperature between 110° and 225° C., contains an appreciably higher proportion of fluorine than that corresponding to the tetrafluoride, and is probably a complex titanium tetrafluoride-amino-ammonium fluoride. To insure complete conversion of the titanium component into the volatile form, ammonium fluoride should be added in considerable excess, 50 per cent or more above the chemically equivalent proportion. The complex compound thus formed below 250° C. begins to volatilize at 290° C. and dissociates into ammonia, ammonium fluoride, and titanium diaminotetrafluoride. Instead of adding ammonium fluoride as such to the charge, a reactive mixture of ammonium sulfate and fluorspar capable of producing it may be employed. Either the normal or acid sulfate may be used. Ammonium fluoride has the advantage that it can be regenerated in the process and that it yields a primary complex titanium tetrafluoride compound which is not attacked by water vapor generated in the reaction.

The primary reaction is carried out at temperatures above 110° C. so that any water formed is removed from the mass, and to aid in maintaining a dry state the reactive fluoride may be added gradually. This avoids any possible accumulation or sintering of the charge. The temperature is maintained below 250° C. during the formation of the primary complex titanium tetrafluoride compound to avoid losses due to dissociation. Any silicon diaminotetrafluoride begins to volatilize at about 230° C., and practically all distills over below 290° C. The reaction product is then heated to 290° to 350° C., at which temperature the primary complex titanium tetrafluoride compound vaporizes and dissociates to form the titanium diaminotetrafluoride, along with other products, which may be condensed and collected. This compound in the vapor phase is contacted with water and ammonia, in excess, to precipitate hydrous titanium oxide. A denser and more readily filtrable form of titania may be obtained by employing an ammoniacal solution of

concentrated ammonium fluoride instead of aqueous ammonia, and by carrying out the reaction at reduced temperatures, the density of the precipitate may be further increased.

The solid residue from the primary reaction, consisting primarily of iron fluoride, is heated with ammonium sulfate at 200° to 250° C. to form ammonium fluoride, which passes off as a vapor, leaving ferrous sulfate. This recovered ammonium fluoride may be dissolved in the solution used in decomposing the titanium diaminotetrafluoride. Losses of ammonium fluoride in the process may be replaced by adding ammonium sulfate and fluorspar to the reaction residue just before its decomposition by ammonium sulfate. Either the normal ammonium fluoride or the bifluoride may be employed with equal success.

As an example of the process, ilmenite ground to pass a 150-mesh screen was heated at 150° to 200° C. in an externally fired enclosed furnace equipped with stirring devices, a feeding arrangement, and outlets for discharge of the vapors and residue, and 2 to 2.5 parts by weight of ammonium fluoride crystals were gradually added over a period of several hours. The ammonia and water vapor liberated were recovered, and after the reaction had gone to completion, evidenced by a change in color of the powdery mass from black to grayish white, the temperature was raised to 350° C. to vaporize and distill off the titanium-fluorine compounds. Ammonium sulfate equal to the weight of the original ore was then added to the residue, and the mixture was heated at 300° to 350° C. to recover the fluoride content as ammonium fluoride, which was distilled off, leaving ferrous sulfate and a small proportion of other metallic sulfates. During this operation a mixture of fluorspar and ammonium sulfate was added to replace mechanical losses of ammonium fluoride in the previous cycle.

The combined furnace vapors, containing titanium tetrafluoride, ammonium fluoride, and ammonia, were led into a spray of ammoniacal ammonium fluoride in a cooled scrubbing tower to effect precipitation of the titanium. The reaction was carried out below 34° C. to obtain better yields, and a denser, more readily filtrable product was obtained at temperatures below 10° C. In general, the density of the precipitate was proportional to the fluoride content of the solution and inversely proportional to the temperature of the scrubber liquor. The titania was separated from the ammoniacal liquor by filtration, washed, dried, and calcined to produce pigment. A part of the filtrate was evaporated to recover crystalline ammonium fluoride, and the ammonia given off was used for regeneration

of ammonium sulfate. Wash water from the filtration step was added to the remainder of the filtrate and the liquor was recirculated.

According to an improved process devised by the same workers, the ore was heated with ammonium fluoride to produce tetrafluoride compounds of titanium and ammonium which were dissolved in water or nonalkaline ammonium fluoride solution.[8] To secure a high yield of these primary compounds, the ammonium fluoride was added to the titaniferous material in excess of the quantity theoretically required for conversion into simple fluorides. Thorough mixing of the ore and reagent was found necessary to insure complete reaction, and this was accomplished by grinding the components in a ball mill or edge-runner mill, or by adding the ammonium fluoride in the form of a concentrated aqueous solution. The water was then driven off and the mass was heated at 150° C. until the reaction proceeded to completion and ammonia ceased to come off. Rutile required a higher temperature than ilmenite, and either normal ammonium fluoride or the bifluoride gave satisfactory results. At this stage the silicon content was volatilized as a diaminotetrafluoride by heating the residue below 290° C., for at this temperature titanium compounds began to distill over. Because of the wide difference in the boiling points of the corresponding fluoride compounds (titanium and silicon), complete separation was effected. Although the reaction mass was kept below 290° C. for a considerable period of time to volatilize as much ammonium fluoride as possible for separate recovery, in general the temperature after reaction at 150° C. was raised as rapidly as possible to 300° C. to cut the operating time and increase the output of the unit.

The titanium was then largely or completely separated from the reaction mass by leaching with water or a nonalkaline solution of ammonium fluoride. In some instances there was excess ammonium fluoride in the reaction product, sufficient to provide part of or all the requirements of the leaching solution, and water or dilute liquor was used. After filtration, to separate the suspended solids, the solution was neutralized with ammonia to the point of incipient precipitation, and treated with a soluble sulfide (ammonium, sodium, potassium, or hydrogen sulfide) at 70° C. to precipitate the iron and other heavy metals present as impurities. If hydrogen sulfide was employed, additional alkali was required to maintain the necessary hydrogen ion concentration. During the precipitation, ammonium sulfide reduced any ferric iron to the ferrous state, and care was taken to prevent reoxidation of this component, since the ferric compound redissolved in the fluoride liquor. This purified solution

was mixed with aqueous ammonia, and the resulting liquor, containing the hydrous titanic oxide in suspension, was cooled to below 34° C. to effect complete precipitation. Denser and more readily filtered titania was obtained by further reducing the temperature to below 10° C. and increasing the concentration of fluorides in the liquor from which it was precipitated. The hydrous oxide was filtered, washed, dried, and calcined, and the filtrate containing ammonium fluoride and ammonium hydroxide was reused in the process.

After leaching the titanium from the primary reaction product, 0.8 parts ammonium sulfate was added to the residue for each part of the original ore, and the mixture was heated to 300° to 350° C. to drive off the ammonium fluoride, which was collected for reuse.

In an actual operation, 100 kg. of finely ground ilmenite was mixed with 400 kg. of ammonium fluoride in the form of a strong aqueous solution and introduced into a closed reaction vessel fitted with a stirrer. The mass was heated to 110° to 180° C. and held at the latter temperature, with agitation, until the reaction had gone to completion. All ammonia, ammonium fluoride, and water vapor liberated were drawn off and collected for recycling. Hot water was then added to the reaction product, and after digestion the insoluble ferrous fluoride was filtered hot from the leach liquor. Ammonia was added to the hot filtrate containing the ammonium tetrafluoride compound just short of the amount required to effect precipitation, and then ammonium sulfide was added to convert the iron and other heavy metals present to insoluble sulfides. These were filtered off and the iron-free solution was diluted with water and introduced into aqueous ammonia to precipitate the titanium as hydrous oxide. If, on the other hand, the ammonium hydroxide was poured into the solution, some of the crystalline complex titanium ammonium fluoride compound formed. The hydrous oxide was filtered, washed, and calcined at 900° C. Ammonia and ammonium fluoride were recovered from the filtrate for use in a later cycle.

The iron double-fluoride residue was heated in the presence of steam in a closed furnace at 400° to 550° C., and the volatilized ammonium fluoride was condensed, leaving residual iron oxide suitable for pigment or abrasive uses. This ordinarily gave a black product, but if a red oxide was desired, the double fluoride was first decomposed at 400° to 450° C., and after volatilization of the ammonium fluoride the residue was heated with moist air at 500° to 550° C. Ammonia and ammonium fluoride produced in the various reactions were collected and used again in the process, so

that in continuous operation it was only necessary to make up for mechanical losses of these materials from time to time. In certain reactions ammonium sulfate was employed, and the process with reference to this reagent was also cyclic.

As already pointed out, the titanium solution obtained by leaching the reaction product of ilmenite with ammonium fluoride usually contains a small proportion of salts of iron and other heavy metals, and unless removed, these impurities would be precipitated with the titanium and have a detrimental effect upon the color and other properties of the resulting pigment. However, by regulating the hydrogen ion concentration of the fluoride solution within narrow limits, the iron may be precipitated quantitatively by adding a soluble sulfide, with no significant loss of titanium." The tendency of the added sulfide to form titanium oxide or other insoluble compound may be depressed further by the presence of an additional soluble fluoride salt such as ammonium fluoride.

To illustrate, finely ground ilmenite was heated with an excess of ammonium fluoride as a concentrated solution, 50 per cent or more above the stoichiometric proportion, until the water had been driven off, and finally at 150° to 180° C. to complete the reaction. This large excess of reagent served the double purpose of insuring complete conversion of the ilmenite into fluorides and of supplying the desired ammonium fluoride to the leach liquor. After the reaction had ceased, the product was lixiviated with water, and the solution of titanium and ammonium fluorides, containing also a small amount of iron fluoride as impurity, was filtered to remove the practically insoluble double fluoride of iron and ammonium. Solutions prepared in this manner were acidic, and before treatment were neutralized with ammonia to the point just short of a permanent precipitate of titanium oxide. This condition corresponded to a pH of approximately 6.8, and it was closely maintained until the insoluble sulfides were removed from the solution. Ammonium sulfide was then added to precipitate the iron and heavy metal compounds. Sodium, potassium, or hydrogen sulfide could be used, however, but if the latter agent was employed additional ammonia was required to maintain the necessary neutrality, otherwise the iron sulfide redissolved. Best results were obtained at 50° to 60° C., and also at this temperature the insoluble sulfides formed were readily removed by filtration. The iron was precipitated as ferrous sulfide, since any ferric ions would be reduced to the ferrous state by the ammonium sulfide, but precautions were taken to prevent reoxidation before or during filtration, for ferric sulfide was soluble in the

fluoride solution. In general the ratio of ammonium fluoride to titanium fluorides in the solution was greater than 1 to 1 but less than 5 to 1, and the specific gravity was 1.110 to 1.125 at 60° C.

Solid particles suspended in an aqueous solution of a titanium fluoride salt, such as is obtained by the reaction of ilmenite with ammonium fluoride, were coagulated so as to facilitate settling and filtration, by agitating the liquor with a small amount of a flocculent titanium compound.[10] Such an agent was prepared by adding sodium phosphate, sodium carbonate, or potassium hydroxide to the fluoride solution, under such conditions that a stable, adsorbent, flocculent precipitate of hydrous titanium phosphate or oxide formed. The precipitate could be formed in place.

Ammonium fluotitanate solution, as obtained in digesting ilmenite with ammonium fluoride, was added to an excess aqueous ammonia to precipitate the titanium as hydrous oxide,[11] or the two solutions were fed simultaneously into the mixing tank.[12]

In a two-stage process,[13] finely pulverized ilmenite was heated with a solution of ammonium fluoride of more than 20 per cent strength under pressure of 2 to 20 atmospheres at the corresponding temperature. More ammonium fluoride was added to replace losses and the reaction product in the form of a slurry was filtered. Titanium hydroxide was precipitated from the solution, filtered, calcined, and milled in the usual manner to yield pigment. The filter cake was heated with 20 per cent ammonium fluoride under pressure, as before. More ammonium fluoride was added to replace losses and the resulting slurry was filtered. The filtrate was used for the initial treatment of a fresh batch of ore.

Titanium dioxide, hydrolytically precipitated from an aqueous solution of titanium fluoride to which had been added a small proportion of sodium citrate, arsenate, or carbonate, gave on calcination a pigment having rutile crystal structure.[14] Improved pigment properties [15] were developed by adding a small proportion of zinc, beryllium, or magnesium sulfate to the filtered and washed pulp before calcination.

According to Svendsen,[16] a pigment consisting of an intimate mixture of titanium dioxide and silica, prepared by coprecipitation from fluoride solutions, had the same characteristics as the pure titanium dioxide product. In decomposing ilmenite or other ores with an excess of acid ammonium fluoride in both the wet and dry procedures, the silica and silicates usually present as impurities were also converted to soluble form. If the reaction was carried out in the dry state, the ammonium tetrafluorides of titanium and silicon

formed were volatilized by heating the reaction mass at temperatures above 270° C., and collected in water to form pure solutions which were treated with ammonia to precipitate the mixed hydroxides. However, if the original reaction product was kept below the temperature of volatilization and the product was leached with water, the titanium and part of the silicon dissolved as fluoride compounds, along with a small amount of iron and other impurities. Heavy metals were precipitated with ammonium sulfide after the liquor had been made almost neutral by adding ammonium hydroxide and the purified solution was added to aqueous ammonia to coprecipitate the hydroxides of titanium and silicon. This procedure was followed to insure the presence of ammonium hydroxide throughout the precipitation step. The mixed hydroxides were filtered, washed, calcined, and pulverized for pigment use.

Individual particles of coprecipitated titania and silica usually had an average diameter of less than 1 micron and ranged down to below 0.25 micron. With silica up to 10 per cent, each separate calcined particle appeared under the microscope as crystallized titanium dioxide, and separate silica particles could not be detected under the most powerful petrographic microscope. The index of refraction of the composition was practically that of pure titanium dioxide, although the specific gravity was substantially lower.

Calcination temperature required to effect crystallization of the titania and develop the required pigmentary properties was found to increase with the proportion of silica, but varied from 850° to 1100° C. For example, with 10 per cent silica the product was heated at 1025° C. for 1 hour to effect anatase crystallization, but if the temperature was raised well above this value, for instance, 1050° C., the product became hard and yellow. With 3 per cent silica, calcination at about 985° C. was sufficient, although with 20 per cent of this component 1045° C. was required. Pure titanium oxide became hard and assumed a gray-brown color even at these temperatures, which seemed to be associated with the rutile crystal modification. The silica in intimate association apparently raised the temperature at which crystallization of the titania component took place. Pigments having from 5 to 15 per cent silica possessed these improved qualities to the highest degree, although this component was in some tests raised to 75 per cent.

A similar pigment containing a smaller proportion of silica was prepared by calcining the composite precipitate obtained by treating an aqueous solution of an alkali fluosilicate of titanium and silicon with ammonium hydroxide.[17] By another approach, pigments of

similar properties were made by blending at least 5 per cent silica with titanium dioxide.[18] Silicon dioxide of the proper texture was produced by calcining the precipitate obtained by treating the solution of an alkali metal fluosilicate with ammonium hydroxide.

By carrying out the hydrolytic precipitation in the presence of small proportions (1 per cent) of such coagulating agents as acids or salts that, under the conditions employed, yielded polyvalent negative radicals or ions, titania of a nonpeptized, flocculated form was obtained, with the result that it was easily filtered and washed.[19] The more effective agents were found to be oxalic, citric, sulfuric, phosphoric, and tartaric acids, and their alkali metal and ammonium salts; these could be added either to the titanium fluoride solution or to the aqueous ammonia used as precipitant. In an actual operation, 4.0 g. of ammonium sulfate was added to 10 kg. of titanium ammonium fluoride solution containing 800 g. titanium dioxide, and this mixture was run into 50 kg. of 10 per cent ammonium hydroxide solution over a period of 40 minutes. The highly flocculated precipitate was washed and calcined at 1000° C. for 2 hours to produce a titanium dioxide pigment of the rutile crystal form possessing superior tinting strength and color.

Ilmenite or rutile, ground to 100 mesh, was heated with K_3FeF_6 or the corresponding compound of nickel, cobalt, or zinc at 700° C. for 1 hour. The sintered product was crushed and leached with water, and the resulting compound, K_2TiF_6, was purified by crystallization and converted to the oxide, chloride, or sulfate of titanium.[20]

Nitrate Process

McKinney[21] reported an interesting process for producing rutile-type pigments, employing nitrate solutions which involved heating anatase titanium dioxide with barium hydroxide to form the titanate, followed by dissolution in nitric acid and reprecipitation by thermal hydrolysis of the solution, after separation of most of the barium nitrate by crystallization. Keats[22] developed a cyclic operation based on this process, according to which the nitric acid and barium hydroxide were recovered and reused. Anatase pigments are produced commercially by processes involving the thermal hydrolysis of sulfuric acid solutions because of the smoothness of operation and relative simplicity of handling such solutions. Since the hiding power of a white pigment is proportional to the refractive index of the particles, it follows that rutile, with an index of refraction of 2.71, will have a higher hiding power than anatase

with a refractive index of 2.55, other factors being equal. From this standpoint the production of rutile pigment is desirable, but methods consuming halide solutions (chlorides and fluorides) are relatively expensive. Furthermore, the dilute hydrochloric acid recovered in the hydrolysis step is, as a general rule, salable in large amounts at prices competitive with sulfuric acid, if at all, and regeneration of chlorine from the liquor would not be economical, since the recovery cost would equal or exceed the original cost of manufacture of chlorine.

This cyclic process avoids the use of halide solutions and the corrosion problem encountered in handling the corresponding acids. Nitric acid is not nearly so corrosive, and plant design is therefore simpler and more economical. This method is largely supplemental to the conventional process based on sulfate solutions, and most of the equipment would remain in use.

Hydrous titanic oxide of the anatase crystal modification, as obtained commercially by the thermal hydrolysis of sulfate solutions of ilmenite, was washed free of iron, neutralized with an alkaline agent, and again washed to remove the salts formed in the reaction. This sulfate-free pulp was suspended in a chemically equivalent amount of aqueous barium hydroxide and heated near the boiling point of the solution to form barium titanate. For each mole of this compound, 5 to 10 moles of nitric acid of 30 to 50 per cent strength was added to form barium nitrate and titanium nitrate. Barium nitrate was only slightly soluble in the strong liquor so that a greater part of it crystallized and was separated readily by decantation, filtration, or centrifuging. The filtrate, consisting largely of titanium nitrate, was adjusted to a concentration of 80 g. to 120 g. titanium dioxide equivalent per liter, and after proper seeding was hydrolyzed by boiling. The precipitate was filtered, washed, and calcined to produce titanium dioxide of pigment grade having the rutile crystal structure. In carrying out the hydrolysis reaction, solutions of concentration above 40 g. titanium dioxide equivalent per liter were used, for otherwise the anatase modification resulted.

The nitric acid filtrate from the hydrolysis product was collected for reuse, and the barium nitrate crystals were decomposed by heat to give oxides of nitrogen and barium oxide, all of which were recovered and used again. The residue of barium oxide was added to water to regenerate the hydroxide and used for attacking another batch of anatase pulp. Chemical reactions involved in the process are as follows:

$$Ba(OH)_2 + TiO_2 \text{ (anatase)} \rightarrow BaTiO_3 + H_2O$$
$$BaTiO_3 + 6HNO_3 \rightarrow Ba(NO_3)_2 + Ti(NO_3)_4 + 3H_2O$$
$$Ba(NO_3)_2 \rightarrow BaO + N_2O_5$$
$$N_2O_5 + H_2O \rightarrow 2HNO_3$$
$$Ti(NO_3)_4 + 2H_2O \rightarrow TiO_2 \text{ (rutile)} + 4HNO_3$$
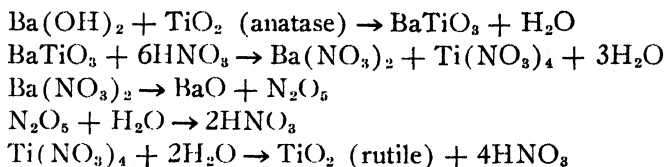
According to a specific procedure, iron-free anatase pulp obtained by the conventional hydrolysis of sulfate solutions of ilmenite was slurried in water, neutralized with ammonium hydroxide, and washed free from sulfates and other salts formed in the reaction. The sulfate-free cake was mixed with a chemically equivalent amount of barium hydroxide in aqueous solution; the slurry was heated to the boiling point and maintained for 1 hour to bring about formation of barium titanate. This reaction product was dewatered and the cake was treated with cold 50 per cent nitric acid, with agitation. After several hours the suspension lost its opalescence and then consisted of crystals of barium nitrate suspended in the solution of titanium nitrate. Upon filtration, 80 per cent of the nitrate solution was recovered before washing, and the remainder by washing with cold acidified, saturated barium nitrate solution. The initial filtrate was combined to give a solution having more than 80 g. titanium dioxide per liter, which was subjected to thermal hydrolysis after addition of a seeding material prepared after the method of Kubelka and Srbek.[23] The precipitate was filtered, washed, and calcined according to accepted methods to produce rutile titanium dioxide of pigment grade.

Sulfide Process

A unique process of producing titanium dioxide, which involved a sulfide stage, was developed by Pipereaut and Helbronner.[24] Ilmenite was heated with coal and sulfuric acid or pyrite in a closed vessel, and the iron was dissolved from the reaction product with dilute sulfuric acid, leaving a titanium dioxide residue which was mixed with coal and subjected to the action of chlorine at a dull red heat. The titanium tetrachloride still in the vapor form was passed with dry hydrogen sulfide through tubes externally heated at 400° C. to form the sulfide. Alternatively, the tetrachloride was condensed and cooled to 100° C., and the hydrogen sulfide was admitted. In either modification the titanium sulfide produced was roasted alone to produce the dioxide or with zinc sulfate to produce

a composite pigment consisting of oxides of titanium and zinc. By carrying out the roasting operation in closed vessels in the absence of oxygen, the zinc component was obtained in the form of sulfide rather than oxide. Fillers such as barium sulfate were added before the last roasting operation to obtain extended pigments.

Similarly, titanium sulfide and hydrochloride acid were produced by the reaction at a dull red heat of a gaseous mixture of *equal volumes of carbon dioxide and hydrogen sulfide with titanium tetrachloride. The sulfide was then calcined to remove the sulfur and roasted to yield titanium dioxide.[25]

Chloroacetate Process

Young [26] prepared the chloroacetate of titanium and heated the compound to 800° C. or above for 2 hours to form the dioxide of the rutile crystal modification. This product had a petal-like structure with a surface area many times that of the initial material, and the coalesced particles were readily broken up by light rubbing.

Chapter 19

TITANIUM PIGMENT INDUSTRY

Development, Plants, and Processes

In 1869, Ryland, in England, pulverized a sample of ilmenite and ground the dried material with a linseed-oil vehicle to produce a black paint. The following year, Overton, in the United States, patented an anti-fouling coating composition for ships' bottoms which was prepared by mixing finely ground rutile in a bituminous material such as tar or pitch. These appear to be the first recorded attempts to utilize titanium compounds as paint pigments, but these pioneer investigators seemed to have entirely missed the advantages of separating the oxide in the pure condition, and it was more than 30 years later before this problem received serious consideration.

About 1870, A. J. Rossi, a young French metallurgist and chemist, came to the United States and successfully smelted titaniferous iron ores at Boonton, New Jersey. As an outgrowth of this work he became very much interested in utilizing the titanium content as such, and he developed methods of producing titanium alloys in the electric furnace. The Titanium Alloy Manufacturing Company was incorporated in 1906, and a plant was built at Niagara Falls, New York, for the production of ferrocarbontitanium according to these processes, to supply the demands of the iron and steel industry. Encouraged by this success, Rossi's interests spread to other fields, and in 1908 he prepared a relatively pure titanium dioxide and proved its high opacity as a pigment by mixing the material with salad oil and brushing out the resulting composition. This was probably the first instance of the use of chemically prepared titanium dioxide as a white pigment.

In 1912 L. E. Barton joined Rossi in a systematic program of research on the pigment possibilities of titanium compounds, and shortly worked out a method of separating the dioxide from ilmenite, titaniferous iron ores, and rutile, and demonstrated the adaptability and outstanding properties of this material. The composite barium sulfate and calcium sulfate pigments, containing 25 per cent titanium dioxide, were conceived by these workers, and development work

355

progressed with such success that the Titanium Pigment Company was organized and a factory was begun at Niagara Falls, New York, in 1916, for large-scale production according to their method. War-time conditions delayed operation, however, and it was not until after the armistice in 1918 that commercial production began. The National Lead Company purchased a substantial interest in the company in 1920, and in 1932 acquired the outstanding shares of common stock. In 1937 the operating units were designated as Titanium Division, National Lead Company, and the name Titanium Pigment Corporation was applied to the sales agent. A second and larger plant was built in St. Louis, Missouri, in 1923 for making the composite pigment. Production of relatively pure (96 to 99 per cent) titanium dioxide was begun at the Niagara Falls plant in 1925, and demand for this pigment soon exceeded the production capacity so that a new factory was built in Sayreville Township, New Jersey, in 1934. The first unit was placed in operation in April, 1935, and the following year the Niagara Falls plant was discontinued. Several additions have since been made to the Sayreville plant.

Very extensive and readily worked deposits of titaniferous magnetites and ilmenite occur near the southwest coast of Norway, and in 1908 a government commission was appointed to investigate the utilization of these ores. Farup and Jebsen first conducted a joint study on the smelting of these ores for iron, and they came to realize the difficulties involved in such an operation. A search for other methods of utilization focused attention on the titanium content, and this investigation led to the development of titanium dioxide pigments. The first product, made from ilmenite and known as titanium ocher, had great opacity but was of a reddish yellow color far short of the desired goal. However, methods for the recovery of pure white titanium dioxide of pigment quality were developed by 1912, and production of the composite pigments on a commercial scale was begun at Fredrikstad almost simultaneously with the initial output in the United States. According to this process, the finely ground ilmenite ore was heated with strong sulfuric acid to produce soluble titanium and iron sulfates, and this was a decided improvement over the fusion methods of Rossi and Barton.

To facilitate the commercial development of the pigments, the American and Norwegian interests, which had worked independently up to this time, came together in 1920 and agreed to a plan for cross licensing of patents and mutual exchange of technical information and operating experience. In 1927 the National Lead Company bought a controlling interest in the original Norwegian company,

Figure 10. Modern titanium pigment plant

357

Titan Co., A.-S., including its ore holdings and French affiliate, Société Industrielle du Titane, a sales company.

Later in the same year an agreement was made with the I. G. Farbenindustrie, A. G., for the formation of a jointly owned German company, Titangesellschaft m.b.H., to supply the European and Asiatic markets. A new manufacturing plant was built at Leverkusen, Germany, to supersede the original Fredrikstad unit, which was abandoned.

In 1933 the British Titan Products Company, Ltd. was organized under the joint ownership of the Titan Company, Inc., a holding company of Delaware, representing the interests of the National Lead Company and Dr. G. Jebsen in the Norwegian, German, and French companies, and several British interests, the Imperial Chemical Industries, Ltd., Imperial Smelting Corporation, Ltd., and Goodlass Wall and Lead Industries, Ltd., for the manufacture and sale of titanium pigments throughout the British Empire except Canada. Production began in 1934.

In connection with certain of its European associates, the Titan Company, Inc., along with Japanese interests, organized the Titan Kogyo Kabushki Kaisha in 1936 and built a plant at Kobe to supply the demand for titanium compounds in the Japanese Empire.[1]

An outline of the commercial manufacturing process for the production of anatase from sulfate solutions was given by Hagar.[2] Finely ground ilmenite ore is mixed in a large tank with concentrated sulfuric acid and heated to initiate the exothermic reaction which proceeds violently to completion within a very short time to give a solid porous digestion cake. This reaction product of soluble sulfates is left in the tank and leached to obtain a solution of titanic, ferrous, and ferric sulfates containing some unreacted ore and siliceous residue in suspension. All ferric component is reduced to the ferrous state with scrap iron, and to prevent later reoxidation a small proportion of titanium is reduced to the trivalent form in the same manner. The liquor is then passed through a series of settling and washing tanks, filtered to remove the last traces of solid materials, adjusted to definite and predetermined concentrations with respect to titanium sulfate, ferrous sulfate, and sulfuric acid, and pumped to storage tanks.

If it is desired to make a composite pigment on a barium sulfate base, the blanc fixe pulp is suspended in the clarified ilmenite solution in such proportions that the finished product will contain 30 per cent titanium dioxide. The solution is then simply boiled until most of the titanium is hydrolytically precipitated upon the extender, and the

slurry, consisting essentially of the composite precipitate suspended in a solution of ferrous sulfate and sulfuric acid, is filtered and washed on a series of especially designed continuous filters. In preparing blanc fixe of the required grade, pulverized barytes is roasted with powdered coal to produce soluble barium sulfide, and this compound is leached from the mass with water. After clarification, aqueous sodium sulfate is added to the solution to precipitate barium sulfate, which is washed and stored for use in the form of a paste or sludge. The concentration and temperature of the solutions must be carefully controlled to produce blanc fixe of the required quality. Sodium sulfide may be recovered from the filtrate as a by-product.

On the other hand, if the pigment is to be made upon a calcium sulfate base, the same general procedure is followed except that a slurry of the anhydrite crystal modification is suspended in the ilmenite solution. The methods of hydrolysis, washing, settling, and filtering are the same, and the final pigment contains 30 per cent titanium dioxide as before. Calcium sulfate employed is prepared by adding lime slurry to strong sulfuric acid under carefully controlled conditions to develop the desired properties and these will be imparted to the finished composite pigment.

Attempts to prepare pure titanium dioxide from such a solution in a similar manner without the extender would result in low yields of a product of poor color, deficient in tinting strength and other pigment properties. However, by careful regulation of the absolute and relative concentration of the different components of the solution (that is, by adjusting the ratio of titanium dioxide to sulfuric acid, removal of part of the ferrous sulfate by crystallization, and subsequent concentration to the desired specific gravity by vacuum evaporation), titanium dioxide of pigment grade can be obtained by thermal hydrolysis after proper nucleation. Nuclei may be added or produced in place by adding the concentrated solution to hot water, under carefully controlled conditions. To produce rutile-type pigments from sulfate solutions, nucleating agents are added which will initiate and direct the hydrolytic precipitation of titanium dioxide of the rutile crystal modification.

Regardless of the method of hydrolysis, the washing, calcination, and finishing steps are similar for all types of pigments. The thoroughly washed pulp is fed from the continuous filters to a rotary oil-fired furnace, where it is dried and finally brought to a temperature of the order of 1000° C. to convert the titanium dioxide from an amorphous form, having an index of refraction of 1.8, to a crystalline modification having an index of refraction of 2.55 or 2.71,

and effect a corresponding increase in tinting strength. Calcination is one of the most important steps in the manufacturing process; too high temperature or too long exposure to a lower temperature may cause the pigment to become gritty and may impair the color and tinting strength, while on the other hand under-calcination usually results in good color, but the tinting strength and covering power may not be brought up to the maximum value. The calcined product is either dry-milled, usually on mills of the ring-roll type, or wet ground in a pebble mill, hydroseparated, dried, and finally disintegrated in a mill of the rotary-hammer type. Composite pigments are in general more amenable to dry-milling, while the relatively pure oxide is usually wet-milled. Regardless of the milling procedure, the product is disintegrated and air floated to such a degree that not more than 0.05 per cent is retained on a 325-mesh screen.

According to Bousquet, Richter, and Allan,[3] in the commercial production of relatively pure titanium dioxide pigment concentrated sulfate solutions are used, in which there is less sulfuric acid than that required to form the normal sulfate of titanium, and from which a considerable portion of the ferrous sulfate has been removed by crystallization. Such solutions are designated "basic" because of the acid deficiency. On the other hand, ilmenite solutions for producing coalesced pigments have an acid content in excess of that corresponding to the normal titanic sulfate, and are lower in titanium and higher in iron (relatively) than those used for precipitation of the pure titanium dioxide.

The titanium dioxide-magnesium silicate pigment is made by thorough and careful blending of 30 parts of titanium dioxide pigment with 70 parts of a selected and treated magnesium silicate. Treatment involves the intimate admixture of a wetting or dispersing agent, such as oleic acid.

To produce lead titanate, equimolecular proportions of litharge and washed hydrous titanic oxide are intimately mixed and reacted together at a high temperature to form a new compound which corresponds to the chemical formula $PbTiO_3$. Because of the method of manufacture, the commercial product contains a small proportion of lead sulfate from the residual sulfuric acid in the pulp. Rigid control of the calcination step is maintained to effect complete combination of the components and to develop optimum pigment properties of the lead titanate formed.

The British Titan Product Co., Ltd., at the plant at Billingham, England, preferred a type of pressure hydrolysis. Finely ground ilmenite is decomposed by heating with concentrated sulfuric acid

in the conventional manner, and the reaction product of soluble titanium and iron sulfates is dissolved in water. Ferric salts are reduced to the ferrous state by introducing scrap iron into the solution, and the liquor is clarified and cooled to remove part of the ferrous sulfate by crystallization. At this stage the basic solution, containing 100 g. titanium dioxide per liter, is vacuum evaporated to a specific gravity of approximately 1.60, heated in an autoclave at a temperature corresponding to a pressure of 20 pounds per square inch, and held at this temperature for 80 minutes to effect hydrolysis. The hydrous titanium dioxide is washed by decantation, treated with 0.6 per cent potassium carbonate, calcined to develop pigmentary properties, and finally milled.[4]

At the Leverkusen plant of the Titangesellschaft m.b.H. before World War II, hydrolysis of titanium sulfate solution was effected by thermal hydrolysis at atmospheric pressure after seeding with externally prepared nuclei. Ilmenite solution prepared in the conventional manner by dissolving the reaction product of finely ground ilmenite with sulfuric acid was reduced, clarified, and crystallized, but not concentrated. It contains about 130 g. titanium dioxide per liter, and 25 per cent less sulfuric acid than the amount required to form the normal sulfate with the titanium. Nuclei were prepared by running a sulfate solution of the above composition into a calcium carbonate slurry sufficient to neutralize 82 per cent of the sulfuric acid present and to throw out of solution 97 per cent of the titanium. The precipitate of titanic acid and calcium sulfate was washed, and sulfuric acid and sodium sulfate were added to bring the ratio of titanium dioxide to sulfuric acid to 2.4 by weight. The slurry was then adjusted to a concentration of 73 g. titanium dioxide per liter, and heated for 18 hours at 55° C., with occasional stirring, and diluted with acidified water to 44.5 g. per liter titanium dioxide. At the same time the acid ratio was increased to 2.1. The slurry was then heated to 85° C. and held at this temperature to develop the nucleating property to the maximum degree, after which it was cooled rapidly to below 40° C.

Regular ilmenite solution of the composition given above was seeded with 5 per cent of this nucleating agent, based on the titanium dioxide content, heated with direct steam to 100° C., and held at this temperature for 3 hours to complete the hydrolysis. The precipitate was filtered, washed, calcined, and milled in the conventional manner.

In Europe, Blumenfeld early turned his attention to the production of relatively pure (96 to 99 per cent) titanium dioxide pig-

ments, and in 1920 he devised an improved method of hydrolysis which now bears his name. Patents were granted in England in 1923 and in the United States in 1924. By 1926 three plants employing this hydrolysis procedure had been built and placed in operation in Europe by the Fabrique de Produits Chimiques et de Mulhouse, in France, by the Montecatini interests in Italy, and by the Verein für Chemische und Metallurgische Produktion in Czechoslovakia.

At about this time the Commercial Pigments Company in the United States concluded a license agreement with the Société de Produits Chimiques des Terres Rares, in France, the European licensee of the Blumenfeld process, and a plant was built at Baltimore, Maryland, in 1927. Production began in 1928, and by 1931 an output of 20,000 tons daily of pure titanium dioxide pigment was reached.[5] In 1932 this company was taken over by the Krebs Pigment and Color Corporation, and in 1943 it became the pigment department of E. I. du Pont de Nemours and Company. The Krebs Pigment and Color Corporation was dissolved.

According to the original process,[6] finely divided ilmenite was digested with strong sulfuric acid and the soluble titanium and iron sulfates were dissolved in water. Metallic iron was introduced to reduce all ferric compounds to the ferrous condition, and the liquor was clarified and filtered to remove the last trace of unreacted ore, siliceous residue, and colloidal suspended matter. Mud separated in this operation was washed in a Dorr classifier to recover titanium and acid values. About four fifths of the iron was removed by crystallization as ferrous sulfate, on cooling. The solution was then concentrated by vacuum evaporation and hydrolyzed by running the hot concentrate into about one third of its volume of hot water, followed by boiling, as specified in the Blumenfeld patents. By this process concentrated ilmenite solutions were hydrolyzed to yield titanium dioxide of the anatase crystal modification possessing excellent pigmentary properties, and a waste liquor from which the sulfuric acid could be recovered economically. Control of this step is very exact, since slight variations in the procedure may produce a gritty product of relatively large particle size, high oil absorption, and low hiding power. The hydrolysis product was separated from the strongly acid liquor by filtration on Sweetland presses, and the filtrate was sent to the contact plant for recovery of sulfuric acid. The titanic oxide cake from the press was repulped, subjected to additional washing operations, and filtered on Oliver continuous filters.

Research workers of E. I. du Pont de Nemours and Company developed a method of producing composite pigments by blending finished titanium dioxide pigment with specially prepared calcium sulfate and barium sulfate. A plant was built at Edge Moor, Delaware, to manufacture these types of pigments, and production began in 1935. This method was designed to develop fully the excellent pigment properties of the titanium dioxide, its full tinting strength and color, and blend it with calcium sulfate or barium sulfate of a grade especially produced to yield the most satisfactory characteristics for pigment use. Blending was normally carried out in the wet state, and the mixture was dried and recalcined, after which it was milled in the conventional manner. As in the coalesced products, the final composition contained 30 per cent titanium dioxide.

The three affiliated European companies operating according to the Blumenfeld process are relatively small; for example, the Italian plant in 1937 produced only 1803 tons of titanium dioxide pigment.[7]

In 1933 the Chemical and Pigment Company (Glidden Company) and the Metal and Thermit Corporation, both of which had been conducting independent research relative to the production of titanium dioxide pigments for a number of years, joined in forming the American Zirconium Corporation for the purpose of manufacturing such pigments.[8] The incorporators had developed new improvements in the manufacturing process, and a plant was constructed in Baltimore, Maryland, and placed in operation in approximately one year. Finely ground ilmenite was thoroughly mixed with strong sulfuric acid and heated to initiate the exothermic reaction, and the soluble titanium and iron sulfates were extracted from the cooled mass with water. Any unreacted ore was separated and returned for further attack with another batch. The liquor was treated with scrap iron to reduce all the ferric component to the ferrous state, clarified and filtered to remove all insoluble material, and concentrated in lead evaporators. Careful analytical control was necessary at this stage to secure particles of optimum size on hydrolysis. After the proper concentration was attained, the titanium dioxide was precipitated hydrolytically by boiling the solution in the presence of catalytic nuclei. The hydrous titanium oxide was separated from the acid mother liquor by filtration. This was one of the costliest steps in the process, but by employing special materials or alloys in the design of the filters and special filter media this problem was solved from an operating standpoint.

The pulp, washed free from iron salts, was fed to a continuous rotary calciner where it was dried and heated to incandescence on

its course. Passage through the kiln requires considerable time, and control of both temperature and atmosphere at every point along the course was important. After being discharged, the material was cooled, ground in a ball mill, passed through a hydroseparater, dewatered, dried, pulverized, and packed for shipment.

In 1933 the Southern Mineral Products Corporation was organized for the purpose of making titanium pigments from the ilmenite obtained, along with rutile and apatite, in mining the nelsonite ores of Virginia. A plant was built at Piney River, Virginia, and placed in operation in 1936, employing the Blumenfeld process of hydrolysis. After overcoming a variety of difficulties, a product of consistently good properties was obtained and output was expanded in 1938. The property was taken over by the Virginia Chemical Corporation, a subsidiary of Interchemical Corporation, and in 1945 this development, together with the pigment plant at Piney River, was sold to the Calco Chemical Company, a division of the American Cyanamid Company.

Early in 1938, the Sherwin-Williams Company bought a plant site at Gloucester, New Jersey, and announced that it would manufacture titanium pigments to complete its control of important paint raw materials. The company acquired control of a number of patents based on fluoride processes and continued work along this line through pilot-plant stages. In 1945 the plant site and developments at Gloucester were sold to the Calco Chemical Company, a division of the American Cyanamid Company.

The Pittsburgh Plate Glass Company became interested in the field around 1940, and a number of patents dealing primarily with various phases of chloride processes have been obtained in recent years. This is in agreement with reports that the company normally has large quantities of low-cost, by-product chlorine.

All the producers in the United States employ ilmenite ore, sulfuric acid solutions, and the Blumenfeld process of hydrolysis for the production of the relatively pure anatase-type pigments. Composite pigments are produced both by coprecipitating and by blending the components.

Rutile-type pigments were placed on the market on a commercial scale in 1941, and have now largely replaced the original anatase products. Such pigments are also produced from sulfate solutions of similar composition, after nucleating with agents which initiate and direct the hydrolytic precipitation of titanium dioxide of the rutile crystal modification. Nuclei of this type are prepared generally from relatively dilute titanic chloride solutions by a process

of partial neutralization and heat treatment, or by peptizing hydrous titanic oxide, as obtained from sulfate solutions by thermal hydrolysis, in dilute hydrochloric acid. Chloride and fluoride processes which yield rutile directly have been developed through the pilot-plant stage. One large manufacturer is reported to employ a process in which the ilmenite ore is smelted in an electric furnace to produce iron and a titanium-rich slag. The slag is chlorinated to produce titanium tetrachloride, which, after careful purification, is oxidized to titanium dioxide of the rutile crystal modification and elemental chlorine.

A second and apparently independent producer in Great Britain is the National Titanium Pigments, Ltd., with two factories. The process employed is based upon the patents issued to B. Laporte, Ltd., National Titanium Pigments, Ltd., and Titanium Ltd. of Canada. Ilmenite ore is ground in a Hardinge mill to 200 mesh and treated in pans with oleum without external heating. The resulting solid cake is leached with water to obtain a solution of titanic, ferrous, and ferric sulfates containing unreacted ore and siliceous sludge in suspension. Scrap iron is introduced to convert all ferric iron to ferrous. The solution is cooled to effect crystallization of ferrous sulfate, and the mixture is then centrifuged and settled in Dorr classifiers to remove solid materials. In the hydrolysis vats, steam is admitted from a perforated coil into the agitated solution, which breaks up into hydrous titanium oxide and sulfuric acid. After reaction is complete, the sludge is washed free from iron on a Dorr-Oliver rotary filter, and dried and calcined in a rotary furnace. Careful control is necessary throughout the operation. The cooled product is then ground in a Raymond mill and passed through a cyclone.[9]

Before World War II an independent producer in Germany, S. E. Goldschmidt and Sons, marketed its product under the trade name of Titanal. An additional plant in France, controlled by the Travancore Company, produced titanium dioxide pigments from ilmenite separated from monazite sands. One plant in Holland, owned by the Van der Lande interests, produced pigments from ilmenite obtained as a by-product in the mining and concentration of placer tin ores in the East Indies.

Two plants in the Union of Soviet Socialist Republics, located at Leningrad and at Jaroslav, employ the Blumenfeld process of hydrolysis.[10] Finely ground titanomagnetite concentrate is converted to soluble form by digestion with strong sulfuric acid; the reaction product is dissolved in water; all the iron component is

reduced to the ferrous condition and the solution is clarified and filtered. At this stage the concentration of titanium dioxide is 120 g. to 150 g. per liter, and the iron is reduced to 25 g. to 30 g. per liter by crystallization as ferrous sulfate, on cooling. These crystals are separated, and the solution is concentrated by vacuum evaporation to 200 g. to 270 g. titanium dioxide equivalent per liter. The acid factor, that is, the ratio of active or potential sulfuric acid to titanium dioxide, is less than that corresponding to the normal salt, generally 2 to 1 by weight. A portion of this concentrated solution to be hydrolyzed is heated to 94° C. and poured, at a uniform rate, in 16 minutes into one fourth to one third its volume of water at 91° C. The temperature of the system gradually increases to 102° C. at the end of the period, and is then raised slowly to the boiling point and held for 5 hours. A marked precipitation occurs after 45 to 50 minutes. The hydrous oxide formed is filtered, washed, calcined, ground, and pulverized.

Before World War II there were five small, independent plants in Asia, three in Japan, operated by Shai Industrial Chemical Company and Dai-Nippon Artificial Fertilizer Company, and two in Australia, operated by Titan Products Ltd., Brooklyn, Victoria.[11]

The control and operating status of the plants in Germany and Japan since the war are uncertain, but since the manufacture of titanium pigments cannot be classed as a munitions or war industry, it may be assumed that production will be allowed to continue. Furthermore, the more important plants are owned at least in part by American and British interests.

Titanium, Ltd. acquired control of the Ivry ilmenite deposits in Canada in 1941, and announced that a plant would be built to utilize these ores for the manufacture of titanium pigments as soon as the demand warranted. In 1945 it was reported that plans were being made to build such a plant at Cap de la Madeleine, Quebec, at an estimated cost of $7,000,000.

A study was made of the feasibility of establishing a titanium pigment industry in Spain,[12] and methods were developed for obtaining the dioxide from hystalite, which involved reacting the ore with sulfuric acid, electrolytic reduction, hydrolysis, calcination, and pulverization.

In 1946 the government of the Native State of Travancore, India, was reported to be making efforts to establish a local pigment industry to derive greater benefits from its extensive deposits of ilmenite ore.[13]

It should be remembered that the production, on a commercial scale, of pure white titanium dioxide having good pigment properties, from ilmenite which contains from 35 to 55 per cent oxides of iron, is one of the most precise of chemical operations, and staffs of high order have failed through long periods of time to master the technique of the interrelated steps. It seems paradoxical that one of the blackest minerals should yield one of the whitest pigments.
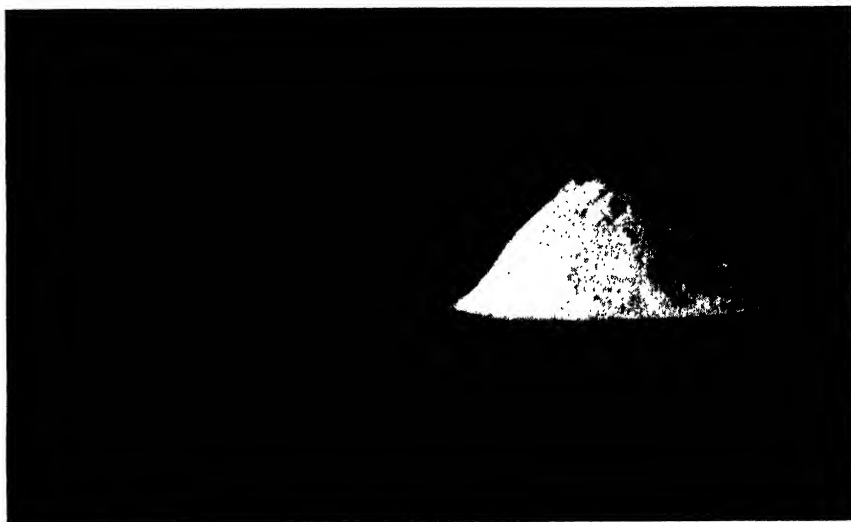
Figure 11. Ilmenite ore and titanium dioxide pigment produced from it
(Reproduced from chapter by author in Volume II of *Protective and Decorative Coatings* by permission of John Wiley and Sons, Inc.)

On July 11, 1945, the District Court of the Southern District of New York sustained the charges brought by the U. S. Department of Justice on June 28, 1943, against the National Lead Company and its subsidiary, the Titan Co., Inc., and E. I. du Pont de Nemours and Company, that the companies participated in a world monopoly controlling the production and sale of titanium pigments in violation of the Sherman Antitrust Act. The U. S. Supreme Court on June 30, 1947, affirmed the judgment and decree of the lower court.[14]

Types of Pigments and Trade Names

The original titanium dioxide pigments were of the anatase crystal modification, but in 1941 rutile-type pigments were placed on the market, and these have largely replaced the older varieties.

In addition to possessing the desirable characteristics of the anatase products, namely, brilliant whiteness, fine particle size, and high chemical stability, the rutile pigments have 30 to 40 per cent higher opacity and greater resistance to chalking and fading. The color of rutile titanium dioxide, although definitely white, has a slightly yellow tone because of somewhat lower reflectance in the violet and blue end of the spectrum and high reflectance throughout the rest of the spectrum.

Commercially available titanium pigments may be arranged according to composition into five main groups, namely, relatively pure, 94 to 99 per cent, titanium dioxide; composites containing 30 per cent titanium dioxide extended with calcium sulfate; 30 per cent titanium dioxide with barium sulfate extender; 30 per cent titanium dioxide extended with magnesium silicate; and 15 per cent titanium dioxide in admixture with a lithopone base. A number of grades of each group have been developed to bring out specific properties to fulfill special requirements, and most of these are available in both the anatase and rutile crystal modifications. In addition there are two main classes of tinted pigments, the relatively pure titanium dioxide colored by calcination with small proportions, usually less than 1 per cent, of oxides of heavy metals such as vanadium, chromium, copper, and manganese, and lead titanate, a yellowish compound, with approximately 36 per cent titanium dioxide in chemical combination with lead oxide.

The first commercial relatively pure titanium dioxide pigment of the rutile crystal modification, produced indirectly by recalcining the anatase product with approximately 1 per cent zinc oxide, exhibited greatly improved resistance to chalking and fading, but this specific property was developed at a sacrifice in hiding power, brightness, and color. It had a tinting strength, as determined by the Reynolds constant volume method,[15] of 1050, brightness of 93 per cent with a yellow undertone, relatively coarse particle size, and maximum resistance to chalking. This product has been largely replaced by a later-developed direct rutile pigment modified with zinc oxide. Trade names: *Ti-Pure 0-600, Titanox-ANC.*

Other pigments of this crystal modification, having from 30 to 40 per cent higher opacity than the best anatase pigment without sacrifice in other properties, were placed on the market early in 1941.

The regular unmodified grade contains approximately 99 per cent titanium dioxide of the rutile form, has an index of refraction of 2.7, specific gravity of 4.2, dry brightness of 97 per cent as com-

pared with magnesium oxide as 100, an average mean aggregate diameter of 0.35 micron, a tinting strength of 1650 by the Reynolds method, and chalking resistance somewhat higher than the corresponding anatase product. Although the pigment is adapted for general use, it is particularly suited for white mixed outside house paints where the free chalking serves to release the free dirt and keep the surface clean. Trade names: *Ti-Pure R-200, Titanox-RA10.*

Another unmodified grade, processed so as to avoid the introduction of coagulating agents, may be readily dispersed in water with a minimum of agitation. It is particularly suited for use in emulsion paints, paper, white leather finishes, shoe cleaners, plastic compounds, soaps, and many other products which require a white opacifying agent in a water vehicle. Trade names: *Ti-Pure R-300, Titanox-RAWD.*

Such a pigment, modified with 0.5 to 1.5 per cent alumina and up to 1.0 per cent silica, exhibits excellent resistance to discoloration on baking and to after-yellowing in baked or air-dried finishes. It has the normal high covering power, brightness, and other properties characteristic of the regular grade rutile. Trade names: *Ti-Pure R-110, Titanox-RA.*

A grade of rutile modified with 1.5 to 2.3 per cent aluminum oxide and 0.6 to 1.0 per cent silicon dioxide shows resistance to discoloration in paint films on aging or baking, has intermediate resistance to chalking and fading, and is of such fine texture that high-gloss enamels can be produced from it with minimum grinding. It has the usual high rutile opacity and brightness. The pigment exhibits sufficient resistance to chalking and fading to be suitable for use in both white and tinted exterior enamels. Trade names: *Ti-Pure R-510, Titanox-RA25.*

Another grade, modified with 0.8 to 1.2 per cent zinc oxide, 0.6 to 1.0 per cent silicon dioxide, and 1.8 to 2.4 per cent aluminum oxide, possesses the highest degree of resistance to chalking and fading of the white titanium pigments, and at the same time retains the covering power, brightness, particle size, and other desirable properties equal to those of the regular unmodified rutile product. It is particularly suited for tinted exterior house paints and enamels, and in white exterior enamels in which a minimum of chalking is required. This pigment is employed in automotive and industrial enamels, floor and deck enamels, and lacquers, where high gloss and maximum fade-resistance are essential. Trade names: *Ti-Pure R-610, Titanox-RANC.*

The regular unmodified anatase pigment contains approximately 99 per cent titanium dioxide. It has a tinting strength of 1275, as determined by the Reynolds method, an index of refraction of 2.55, dry brightness of 98.5 as compared with magnesium oxide as 100, a specific gravity of 3.9, an average mean aggregate particle diameter of 0.3 micron, and poor resistance to chalking, fading, and discoloration. Although suitable for general use, in white mixed house paints the free chalking characteristic makes it effective in keeping the surface clean and white. Trade names: *Titanox-A, Ti-Pure FF*.

A special grade, containing 0.8 to 1.2 per cent alumina as a coating agent, shows somewhat improved resistance to chalking and gives a minimum of discoloration in resin vehicles under conditions of both air-drying and baking. In fact, such films actually bleach on exposure to diffused light. Other important properties, such as covering power, color, brightness, and particle size, are the same as those of the regular untreated anatase product. It is particularly applicable in the formulation of baking enamels for inside use, such as refrigerators, cabinets, appliances, and special architectural finishes. Trade names: *Titanox-A168*.

Another grade, modified with 0.8 to 1.2 per cent antimony trioxide in combination and 0.8 to 1.2 per cent aluminum oxide as a coating agent, has appreciably increased resistance to chalking and fading and at the same time retains the normal anatase opacity and brightness, although it has a slightly yellowish tone. Resistance to discoloration is high. In offset inks it exhibits excellent resistance to leaching in contact with water under conditions encountered in printing. Preferred applications are in white house paints, interior and exterior architectural and household finishes, and automotive finishes. Trade names: *Titanox-AA, Ti-Pure Y-CR*.

Another pigment of this type, made on the antimony trioxide modified base and containing 0.8 to 1.2 per cent of this constituent along with 0.8 to 1.2 per cent aluminum oxide and 0.05 per cent chromic oxide, is one of the most chalk resistant of the high tinting strength, white anatase pigments, and possesses a high resistance to discoloration. The chromic oxide has no noticeable effect upon the color, and the properties are equal to those of the best anatase materials. It may be used in white and tinted coatings such as house paints, interior and exterior enamels, and automotive and industrial finishes. Trade name: *Titanox-A24*.

Still another grade, developed to supply the demand for a pigment that will disperse readily and remain well suspended in

aqueous media, is finished in such a manner as to prevent contamination with even small proportions of coagulating agents such as polyvalent negative radicals or ions. This may be accomplished by employing a dry-grinding process or a special wet-milling operation. It may be used in all aqueous media in which high dispersion is required, as water paints, paper, rayon, and leather finishes. Trade names: *Titanox-AWD, Ti-Pure LW*.

The regular calcium sulfate composite pigment, containing 30 per cent titanium dioxide of the rutile crystal modification and up to 1.0 per cent zinc oxide, retains the desirable characteristics of the older anatase grade and has the added advantage of 20 to 40 per cent increase in hiding power. Expressed quantitatively, the pigment has a tinting strength of 620, dry brightness of 97.5 to 98.5 per cent, specific gravity of 3.25, and effective index of refraction of 1.98. The presence of the rutile form of titanium dioxide gives it a slightly higher specific gravity. It is an all-utility pigment, suitable for use in flat wall paints, enamels, print paints for felt-base floor coverings, paper coatings, rubber, and outside paints where chalking is desired for cleaning the surface. Trade names: *Titanox-RCHT, Ti-Cal R-20*.

A special grade having improved texture and easier grinding properties is particularly suited for gloss paints and enamels. Opacity and other properties are equal to those of the regular grade product. Trade name: *Ti-Cal R-21*.

A grade similar to the other rutile composites, but showing very low water sensitivity, may be incorporated easily and quickly in most vehicles and is of particular value for use in hot humid weather when the regular grade pigments might become too thick and puffy. Trade name: *Ti-Cal R-25*.

Another of the rutile-calcium sulfate composites, having high oil absorption and thick consistency, is exceptionally useful in producing heavy-bodied flat paints. It can be used to advantage in preparing flat paints of normal consistency by reducing the proportion of pigment. Trade name: *Ti-Cal R-30*.

Such a pigment, processed to obtain easy mixing and grinding, fine texture, and maximum degree of dispersion, is designed for gloss paints and enamels. Other properties are not changed. Trade names: *Titanox-RCHTX, Ti-Cal R-31*.

An especially chalk-resistant grade with superior nonfading properties in tints contains 30 per cent rutile titanium dioxide and up to 1.2 per cent zinc oxide extended with calcium sulfate. These outstanding properties are developed at little or no sacrifice in the

other properties, such as opacity, particle size, and color. The pigment is well suited for use in white and tinted exterior paints and enamels, such as ready-mixed house paints, porch enamels, bulletin colors, and exterior industrial finishes in general. Trade names: *Titanox-RC, Ti-Cal R-60.*

The regular anatase-calcium sulfate composite pigment contains 30 per cent titanium dioxide of the anatase crystal modification, has a tinting strength of 470, dry brightness of 99 per cent, effective index of refraction of 1.87, and specific gravity of 3.13. Chalking resistance is relatively low. It is suitable for use in flat wall paints, undercoaters, primers, mill-white glosses and long-oil enamels, rubber, paper coatings, artificial leather, and linoleum. Trade names: *Titanox-C, Ti-Cal SF-101.*

The regular titanium-barium pigment contains 30 per cent titanium dioxide of the anatase crystal modification and approximately 70 per cent of a specially prepared barium sulfate; small proportions of unconsequential impurities are usually present. It has a tinting strength of 440, dry brightness of 98.5 per cent, index of refraction of 1.91, and a specific gravity of 4.24. Pigments of this type find their chief use in mixed white house paints, primers, traffic paints, undercoaters, paper filling and coating, leather finishes, shoe cleaners, linoleum, and oilcloth. Trade names: *Titanox-B30, Ti-Bar HH.*

A special grade of this composite,.containing a small proportion of a wetting agent, possesses the specific property of excellent suspension in all types of paint vehicles and of resisting caking and settling on storage. Other characteristics are retained. Trade name: *Ti-Bar HH-K.*

Another grade which readily disperses in water or aqueous media contains a small proportion of a wetting agent. It is particularly suited for paper filling and coating, leather finishes, emulsion paints, and textile finishes. Trade names: *Titanox-B30WD, Ti-Bar HH-W.*

Such a barium sulfate-anatase composite, containing 30 per cent titanium dioxide and modified with approximately 1.0 per cent antimony trioxide and approximately 1.0 per cent aluminum oxide, has intermediate resistance to chalking and fading and very high resistance to yellowing of enamel films. Opacity, brightness, color, and other important properties remain the same as for the regular unmodified product. It is applicable for exterior enamels and interior quick-drying enamels. Trade names: *Titanox-B30AA, Ti-Bar Y-CR.*

The magnesium silicate composite pigment, like those extended with barium sulfate, contains 30 per cent titanium dioxide of the anatase crystal modification. It has a tinting strength of 440, dry brightness of 96, specific gravity of 3.10, and effective index of refraction of 1.89. Its chief application is in paints containing white lead and zinc oxide, where it serves to improve the appearance and impart greatly increased durability. Trade name: *Ti-Sil*.

Titanated lithopone, containing 15 per cent titanium dioxide, has a tinting strength 50 to 70 per cent higher than that of the unmodified material, as well as improved color and brightness. Such pigments are available in a number of grades, including a water-dispersing product for use in water paints and similar compositions. Trade name: *Ti-Tone*.

Tinted pigments of light gray, dark gray, and light buff shades contain approximately 98 per cent titanium dioxide, together with up to 1.0 per cent metallic oxides in combination as coloring agents. Properties other than color are not influenced appreciably by this treatment so that the high covering power is retained. The pigments have high resistance to chalking and fading and find their chief application in tinted enamels and paints for outdoor service. Trade names: *Ti-Tint LG, Ti-Tint DG, Ti-Tint LB*.

A unique member of the family of titanium pigments is lead titanate in which the titanium dioxide is in chemical combination. The compound corresponds to the formula $PbTiO_3$, although the commercial product contains approximately 7 per cent lead sulfate formed incidental to the manufacturing process. It is of a pale yellow color; has a tinting strength of 570, specific gravity of 7.3, index of refraction of 2.7, dry brightness of 91 per cent, and an ultraviolet absorption of 100 per cent. It retards fading, chalking, checking, cracking, and flaking of paints, and imparts maximum durability to outside coatings of all types. The chief applications are in tinted house paints and porch and deck enamels. Trade name: *Titanox-L*.[16]

Production

In the United States, titanium pigments are produced by the National Lead Company, Titanium Division, in two plants, located at Sayreville, New Jersey, and at St. Louis, Missouri; by E. I. du Pont de Nemours and Company, Pigments Department, in two plants located at Baltimore, Maryland, and at Edge Moor, Delaware; by the Glidden Company (American Zirconium Company) in one plant at Baltimore, Maryland; and by the Calco Chemical

Company, a division of the American Cyanamid Company, in two plants located at Piney River, Virginia, and at Gloucester, New Jersey. The latter three plants are relatively small.

TABLE 12

Estimated Production of Titanium Pigment in the United States in Tons of Processed Titanium Dioxide

Year	Domestic Production of Ilmenite, in tons	Imports of Ilmenite, in tons	Titanium Dioxide Pigment, in tons
1925	5,600	5,000	4,000
1930	2,000	22,298	11,000
1935	10,000	115,871	58,000
1936	10,000	119,922	60,000
1937	10,000	153,971	76,000
1938	10,000	205,000	98,000
1939	13,247	259,419	100,000
1940	18,750	197,759	100,000
1941	21,135	170,689	78,000
1942	70,042	10,369	75,000
1943	184,657	78,092	109,000
1944	252,749	108,948	150,000
1945	308,516	210,066	220,000
1946	282,427	242,826	225,000
1947	336,061	307,735	275,000

Although the individual companies do not give out production figures, they are jointly responsible for a major portion of the world's total. During 1934 the output was placed by independent sources at 32,000 tons,[17] and Hess estimated that in 1937 these companies produced 75,000 tons of processed titanium dioxide out of a world total of 100,000 tons. Hagar [18] reported that even during the depression years, from 1929 to 1935 with the exception of 1932, the yearly increase in sales of titanium pigments was from 20 to 35 per cent, and in the exception noted, tonnage sales were just about equal to those of the previous year. The annual production may be estimated closely from the domestic production and imports of ilmenite ores. In 1939 and 1940, part of the ore imported was not used currently but went to build up stocks in anticipation of the war. In recent years probably 98 per cent of the ilmenite went into the manufacture of pigments, and before the war this value was 90 per cent or higher. The domestic ore contained approximately 44 per cent titanium dioxide, and the imported ore approximately 54 per cent. It seemed safe to assume a 90 per cent

recovery. With these assumptions, the production of processed titanium dioxide was calculated and tabulated as shown in Table 12. Figures for the years since the war are somewhat high because some of the ore was stored as a reserve.

The U. S. Bureau of Mines estimated the titanium dioxide content of ilmenite consumed in the United States in pigment manufacture as 147,905 tons in 1941, 134,968 tons in 1942, 137,399 tons in 1943, 170,518 tons in 1944, and 183,195 tons in 1945.[19] Titanium dioxide amounts to more than 40 per cent of the total white pigment production. E. I. du Pont de Nemours and Company is the largest producer of pure titanium dioxide pigments, while the National Lead Company leads in the manufacture of composite pigments.[20] By far the most important composite pigment is that composed of 70 per cent calcium sulfate and 30 per cent rutile-type titanium dioxide.

Chapter 20

USES OF TITANIUM PIGMENTS

The principal uses of titanium dioxide pigments are in paints, enamels, lacquers, paper, rubber, floor coverings, leather, textiles, welding rod coatings, oilcloth, cosmetics, and plastics. An estimate of the proportion of the total normal consumption in the more important industries is given in Table 13.

TABLE 13

ESTIMATED CONSUMPTION OF TITANIUM DIOXIDE PIGMENTS BY INDUSTRIES [1]

Industry	Per Cent of Total Normal Consumption
Paint, enamel, and lacquer	75
Paper	10
Rubber	2
Floor coverings	2
Leather	2
Textiles	1.5
Welding rod coatings	1.5
Others	6

Paints

Titanium dioxide pigments have many properties which particularly recommend them for use in paints, enamels, and lacquers, and it is in this industry that they find the largest application.

OPACITY. The most evident and striking properties of titanium dioxide are high opacity and covering power. Opacity of a white material is a function of both the index of refraction and particle size, and although the latter may be controlled to a large extent in the manufacturing process, the index of refraction is constant for any specific crystal. Titanium dioxide has the highest index of refraction of any white crystalline material available for pigment use, and the theoretical conclusion that it should have the highest opacity and covering power is borne out in actual practice.

With a given material, covering power, as a rule, increases with decreasing particle size up to a maximum value, and falls off as

376

the fineness of subdivision is carried beyond this point. As the diameter of the individual pigment particles is reduced below the shortest wave length of visible light, approximately 0.4 micron, a diffraction phenomenon occurs and makes the system appear more permeable to light.

Like all other electromagnetic radiations, light waves travel at the enormous velocity of 186,000 miles a second in a vacuum or free space. In transparent materials such as water, glass, and rutile, the speed is diminished and the ratio of the velocity in a vacuum to that in a given material is known as the index of refraction of the material. Inasmuch as the velocity of light is less in a material medium than in free space, a wave front incident upon the boundary of such a medium will be deviated or refracted. From a practical standpoint, change in direction of the light beam is more readily measured than its velocity, and this property is used to determine the index of refraction of the material. The index of refraction may be expressed quantitatively by the equation

$$n = \frac{\sin i}{\sin r}$$

where i is the angle of incidence, or the angle the light ray makes in vacuum with the normal to the surface of contact, and where r is the angle of refraction.

With an aggregation of pigment particles, as in a paint film, light is reflected both by the surface and by the many pigment-vehicle interfaces in the interior. The efficiency of these interfaces depends upon the difference between the refractive indices of the pigment and vehicle, and to a minor extent upon the particle size and the percentage of pigment present. If the medium is linseed oil with an index of refraction of approximately 1.5, 4 per cent of the incident beam will be reflected at the boundary surface between the air and the film; this accounts for the gloss characteristics of the paint. A film with smooth surface reflects the light uniformly (specularly) and is therefore glossy, while one with a rough surface scatters the light in all directions and as a result has a dull or matte appearance. The fate of the remaining 96 per cent of the light that enters the paint film determines the opacity of the system. If the pigment particles have the same index of refraction as the vehicle, there will be no reflection or refraction at the interfaces, and light beams will pass through the composition as though the particles were not present and be reflected or absorbed by the background. Such a composition is transparent because the background

is visible through the film. On the other hand, if the pigment particles have a higher index of refraction than the vehicle, reflection takes place at every surface of contact and the proportion of light reflected at each interface increases with increase in the difference between these values. If the degree of pigmentation and thickness of the layer are sufficiently great, all the light is reflected before reaching the background, the surface on which the coating composition is applied cannot be seen, and the film is opaque.[2] (See Table 14.)

TABLE 14

INDICES OF REFRACTION OF SOME COMMON WHITE MATERIALS

Material	Index of Refraction	Material	Index of Refraction
Vacuum	1.0000	Barium sulfate	1.64
Air	1.0003	Basic lead sulfate	1.93
Water	1.335	Basic lead carbonate	2.00
Linseed oil	1.49	Zinc oxide	2.02
Tung oil	1.52	Antimony trioxide	2.20
Cellulose	1.53	Zirconium oxide	2.20
Clay	1.55	Zinc sulfide	2.37
Quartz	1.55	Diamond	2.47
Calcite	1.56	Titanium dioxide (anatase)	2.55
Talc	1.57	Titanium dioxide (rutile)	2.71
Anhydrite	1.58		

The average tinting strengths of the common white pigments, as determined by the Reynolds constant volume method,[3] are shown in Table 15.

TABLE 15

AVERAGE TINTING STRENGTHS OF SOME COMMON WHITE PIGMENTS

Pigment	Tinting Strength
Titanium dioxide (rutile)	1650
Titanium dioxide (anatase)	1275
Zinc sulfide	850
Titanium dioxide-calcium sulfate composite (rutile)	600
Titanium dioxide-calcium sulfate composite (anatase)	470
Titanium dioxide-barium sulfate composite (anatase)	440
Titanium dioxide-magnesium silicate composite (anatase)	440
Lithopone (high strength)	425
Lithopone (regular)	280
White lead (high strength)	240
Zinc oxide	170
White lead (regular)	140

Hiding power of a white pigment is its capacity to cover a dark surface completely so that the surface appears white, and is expressed as the number of square feet of dull black surface which can be covered completely with 1 pound of the pigment in a paint vehicle, usually linseed oil. Brush-out methods which approximate the conditions of practice do not give very exact values and cannot be carried out with a little sample in a short time, so that quite a number of apparatuses and physical methods have been developed for the measurement of this property. The simple wedge method of Wolff, and the Oswald and the Pfund cryptometers are closest to the principle of the painting method. Usually a parallelism exists between hiding power and tinting strength of white pigments, but it cannot be generalized. Although the index of refraction and particle size of a pigment are the most important factors in determining its hiding power, other properties exert an influence and must be considered. For instance, high brightness (total reflection) as well as low oil absorption contribute to hiding power. A unit weight of pigment will hide increasingly greater areas as its concentration in the vehicle decreases.

The approximate hiding power of a number of common white pigments, expressed as square feet of surface per pound of pigment, is given in Table 16.

TABLE 16

HIDING POWER OF SOME COMMON WHITE PIGMENTS

Pigment	Hiding Power (sq. ft. per pound)
Titanium dioxide (rutile)	220
Titanium dioxide (anatase)	170
Zinc sulfide	108
Titanium dioxide-calcium sulfate composite (rutile)	100
Titanium dioxide-calcium sulfate composite (anatase)	74
Lithopone (high strength)	67
Titanium dioxide-barium sulfate composite (anatase)	58
Titanium dioxide-magnesium silicate composite (anatase)	55
Lithopone (regular)	43
White lead (high strength)	34
Zinc oxide	28
White lead (regular)	20

BRIGHTNESS. Titanium dioxide pigments have light-reflecting values which approach that of magnesium oxide, the universally accepted standard, and values of 96 to 98 per cent are generally

obtained. With the exception of lead titanate, which has a yellowish cast, the brightness readings across the spectrum give results which fall on a straight line. Because of this high total brightness combined with great opacity, these pigments produce clear color tones free from muddiness or undesirable undertones in tinting bases.

CHEMICAL INACTIVITY. As a consequence of its chemical inactivity, titanium dioxide may be used with practically all types of reactive vehicles without danger of thickening, livering, or other undesirable change. It is not discolored by any gases likely to be present in the atmosphere, such as hydrogen sulfide and ammonia. The pigment does not darken or discolor on exposure to the sunlight, and it is indifferent to extremes of temperature; films pigmented with this material can be subjected to high baking temperatures without reaction or alteration. Titanium dioxide is compatible with all types of rosin, resins, gums, and solvents, and gives satisfactory results in all compositions with these materials.

Chemical inertness contributes to stability of the finished paint and to freedom from progressive reactions which might result in ropiness, livering, and other undesirable changes in the container. Because of the absence of soap formation or other reaction with the vehicle, paints pigmented with this agent show improved flow and leveling as compared with similar products containing chemically active white pigments. This property also contributes to the production of paint films of superior smoothness and uniformity. Titanium dioxide is resistant to acid, alkaline, and saline solutions and may be used as the pigment in chemical-resistant paints. It is compatible with other white and colored pigments and may be used safely in combination with these.

Scheiber [4] determined the resistance to corrosion of linseed oil films on platinum and iron electrodes in water by measuring the change of their electrical resistance. The results indicated that such films, pigmented with titanium dioxide, showed greatly improved resistance to corrosion.

SPECIFIC GRAVITY. Titanium dioxide has a relatively low specific gravity, and this property is of economic importance in formulation, for pigments are bought by the pound and the finished paints, enamels, and lacquers are normally sold by the gallon. Obviously the volume cost is an important factor in this field. For example, the volume of a unit weight of anatase titanium dioxide of specific gravity 3.9 is 1.7 times that of basic lead carbonate of specific gravity 6.7. The composite rutile titanium dioxide-calcium sulfate

pigment, with a specific gravity of 3.25, will occupy approximately twice the volume of an equal weight of basic lead carbonate. Because of the low specific gravity, the rate of settling in finished pigments is unusually low.

A comparison of the specific gravity of a number of common white pigments is shown in Table 17.

TABLE 17

COMPARISON OF SPECIFIC GRAVITY OF SOME COMMON WHITE PIGMENTS

Pigment	Specific Gravity
Titanium dioxide-magnesium silicate (anatase)	3.10
Titanium dioxide-calcium sulfate (anatase)	3.13
Titanium dioxide-calcium sulfate (rutile)	3.25
Titanium dioxide (anatase)	3.9
Zinc sulfide	4.0
Titanium dioxide (rutile)	4.2
Lithopone (high strength)	4.2
Titanium dioxide-barium sulfate (anatase)	4.24
Lithopone (regular)	4.30
Zinc oxide	5.65
Antimony trioxide	5.75
Lead sulfate (basic)	6.40
Lead carbonate (basic)	6.70
Lead titanate (yellow)	7.30
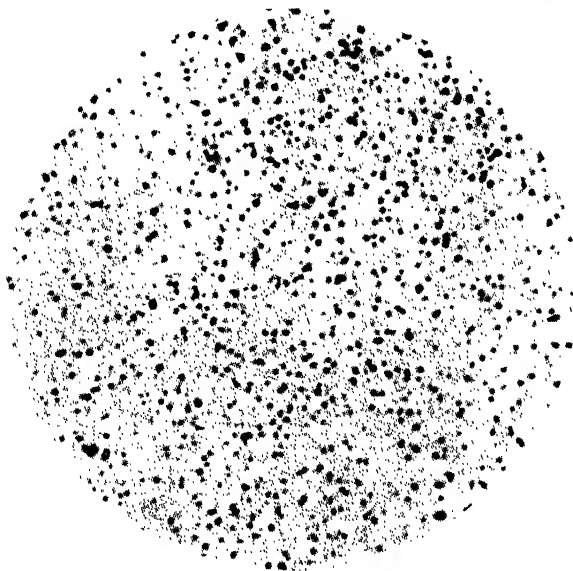
Figure 12.   Photomicrograph of unmodified titanium dioxide pigment, × 1250

PARTICLE SIZE. The aggregate particles of pigment-grade titanium dioxide have a mean diameter of 0.3 micron, although separate crystals are about 0.18 micron. However, the particle size distribution obtainable under actual conditions of coating composition formulation is of more practical importance, and the measured values for regular-grade titanium dioxide dispersed in a paint vehicle are set out in Table 18.[5]

TABLE 18

PARTICLE SIZE DISTRIBUTION OF REGULAR-GRADE TITANIUM DIOXIDE PIGMENT DISPERSED IN A PAINT VEHICLE

Diameter of Particle in Micron	Per Cent by Weight
Greater than 0.5	3
0.5 to 0.4	17
0.4 to 0.3	38
0.3 to 0.2	26
0.2 to 0.15	16

Thus, under these conditions, the most frequent particle size is between 0.3 and 0.4 micron, which approximates the wave length of the lower limit of visible light. Particles larger than 0.5 micron account for only 3 per cent of the total weight.

Dispersed in water, there is a greater proportion of larger aggregates, although the fraction between 0.5 and 0.2 micron is almost constant.

TABLE 19

PARTICLE SIZE DISTRIBUTION OF REGULAR-GRADE TITANIUM DIOXIDE PIGMENT SUSPENDED IN WATER

Diameter of Aggregates in Microns	Per Cent by Weight
44 to 7	negligible
7 to 3	2
3 to 1	5
1 to 0.5	18
0.5 to 0.2	74
Below 0.2	0.6

Jacobsen and Sullivan [6] compared centrifugal sedimentation method for particle-size distribution of titanium dioxide pigment in paint vehicles with values obtained with the electron microscope. Electron micrographs showed that the pigment particles were aggregates, and that milling and the nature of the vehicle affected the size of the aggregates and changed the particle-size distribution. The electron microscope indicated particle shape and specific sur-

face more accurately than sedimentation. Similar studies, employing the electron microscope, were made by Tilleard and Smith and by Hillies.[7]

Moore [8] pointed out the value of crystal chemistry in the study of pigments and pigment-producing minerals.

Because of the relatively coarse nature of the extenders, the barium sulfate and calcium sulfate base composites have an average mean particle size diameter of 0.55 micron, although the individual particles vary in dimension from submicroscopic to a little more than 1 micron. Average mean diameter of the titanium-magnesium pigment is about 1.7 microns, although an average value is difficult to establish, because of the large variations in the particle size of the magnesium silicate extender. The average mean diameter of the aggregates of lead titanate is about the same as that of the pure oxide, 0.3 micron.

APPLICATIONS. Titanium pigments are used in nearly all makes of white enamels and paints for inside use, and they replace part of the other pigments in most high-quality, ready-mixed house paints. Special grades are employed in white and tinted outside enamels and paints.

The relatively pure titanium dioxide pigment is widely used in coating compositions requiring a minimum amount of pigmentation for best results. The small proportions required to provide adequate hiding in enamels, particularly those of the nitrocellulose type, contribute materially to improvement in elasticity, continuity, and gloss of the film.

Lacquers have been successfully pigmented with as little as 6 to 8 ounces per gallon, and oleoresinous enamels rarely require more than 2 pounds per gallon. Titanium dioxide has proved valuable in the formulation of quick-drying coating compositions employing phenol-formaldehyde and alkyd resin vehicles.

It is widely used in oleoresinous and synthetic resin enamels of both the air-drying and baking types, and in metal and decorating coatings. It is a very good pigment for various types of chemical-resistant paints and compositions. It finds wide application, along with the reactive pigments, in the better grades of ready-mixed house paint. Titanium dioxide is well suited for chlorinated rubber coating compositions, and "dienol" waste products from the production of synthetic rubber pigmented with it can be used for acid resisting enamels.

In white baking enamels for inside service, as, for example, on refrigerators where it is necessary to obtain the whitest possible

finish and one that will retain gloss, it is essential that the pigment volume concentration be low, but, at the same time, high opacity must be produced. A special grade of alumina-treated pigment developed for this use produces maximum whiteness and color retention; in fact, such films will actually bleach upon exposure to diffused light.

In exterior white sign enamels of the baking or air-drying type where high chalking resistance is of prime importance although good color and high covering power also are essential, the special zinc oxide and antimony trioxide modified grades are well suited. The very chalk-resistant, rutile-type titanium dioxide (zinc treated) is widely used in exterior enamels, and it offers markedly superior properties for tints.

Paint films pigmented with regular or unmodified titanium dioxide alone chalk so rapidly in outdoor service that the thickness is soon diminished to an undesirable extent. By combining it with zinc oxide and white lead in the proper proportions, however, chalking may be effectively reduced to a minute amount which exerts the desirable property of keeping the surface clean and white. At the same time, cracking, scaling, and checking, failures characteristic of the reactive pigments, can be minimized or entirely eliminated. After years of service, this gradual chalking process leaves the surface in excellent condition for repainting. Erosion proceeds so slowly that the reduction in the thickness of the film is hardly noticeable. As the action proceeds, tiny particles of the pigment separate from the surface and are washed away together with the accumulated dust and dirt by the ensuing rains, leaving a clean white surface.

The composite titanium dioxide-barium sulfate pigments are used in quick-drying household, architectural, and industrial enamels, in baking enamels of all kinds, in metal and decorative coatings, and as a constituent of white paints for outside use.

The principal applications of the calcium sulfate base composites are in all types of interior finishes in which white pigments are employed, such as enamel undercoaters, wall primers and sealers, flat wall paints, interior semigloss and gloss paints, architectural and quick-drying enamels, and eggshell interior finishes. Certain products of the rutile type have greatly increased resistance to chalking, and, in addition to the above-mentioned applications, are used in porch and deck enamels, exterior house paints for both white and tint bases, trim and trellis paints, and in general-purpose enamels for use on either interior or exterior surfaces.

The magnesium silicate-extended pigment finds application in exterior white paste and ready-mixed house paint, and in interior flat wall and semigloss paints. It offers certain advantages over the other composite pigments in that it contributes to exterior paints unusual resistance to checking and cracking. This property is ascribed to the fibrous nature of the magnesium silicate which forms an interlocking structure in the dried film and acts somewhat as a reinforcement.

Titanated lithopones are used in enamels and in flat and exterior paints. The latter compositions, in addition to possessing marked architectural beauty, exhibit long life and leave the surface in excellent condition for repainting.

Because of its extreme resistance to chalking and fading of colors, lead titanate is used primarily in tinted paints and enamels for outside service. While a satisfactory white may carry a considerable percentage of chalk and maintain a slow chalking rate, this condition would cause serious masking of tints.

Caking of titanium dioxide pigments in drying oil vehicles can be prevented by depositing upon the individual particles from 0.25 to 5.0 per cent of a dispersion control agent consisting of one of the acid esters of a polycarboxylic acid with an aliphatic monohydric alcohol having at least eight carbon atoms in the molecule.[9] A typical compound of this group is dodecyl acid phthalate or a salt thereof.

In an example, 100 parts of titanium dioxide was slurried in 400 parts of water and 1 part of dodecyl acid succinate dissolved in dilute ammonium hydroxide was added, with vigorous stirring. The slurry was then treated with dilute hydrochloric acid to regenerate the acid ester, and the mixture was filtered, washed, dried, and pulverized for pigment use. Alternatively, 100 parts of titanium dioxide was stirred into 400 parts of water, and 1 part of dodecyl acid citrate dissolved in the minimum amount of acetone was added slowly, with agitation. As the acetone was diluted, the agent precipitated in a finely divided form which adhered to the surface of the pigment particles. As before, the coated product was filtered, washed, dried, and pulverized.

O'Brien[10] found that titanium dioxide coated with a protective colloid formed a smooth, easy-working composition that was free from agglomerates. Pigments treated in this manner remained in suspension in the vehicle for a much longer period of time. The most effective agents were found to be fatty acids with not over 18 carbon atoms, such as oleic, stearic, palmitic, and lauric, and alkali

or alkaline earth salts of alginic acids. These agents were added in the molten condition or as emulsions in water in proportions from 0.05 to 1 per cent, although in general 0.1 per cent gave optimum results.

The spreading, coloring, and covering power of wall paints containing titanium pigments was improved by imparting wetting agents such as higher sulfonated alcohols in the original composition.[11]

The excellent adhesion of titanium dioxide pigments to wooden surfaces has led to their application in the preparation of priming paints for outside use. Surface coats applied over primers of this type exhibited increased durability, and the failures characteristic of the active type pigments were minimized. Undercoats for protective surfaces of aluminum may be pigmented with titanium dioxide.[12] Since it is essential that luminous paints be applied over a good neutral undercoat, titanium pigments were found to be best for this purpose.[13]

The time required for linseed oil containing cobalt naphthenate to dry to constant weight in actinic light was shortest for unpigmented films and was increased by incorporation of white lead, zinc oxide, and titanium dioxide, in the order named.[14] This trend suggested that the natural antioxidant of the oil was destroyed by the light, but that the opacity of the film retarded this action.

In certain types of coating compositions, particularly water paints, the outside layer of pigment particles of the film in contact with air constitutes the reflecting interfaces; because of the very low index of refraction of air, such materials as calcium carbonate, having relatively low indices, give a satisfactory degree of opacity. Even in such compositions, however, titanium dioxide would be more effective, since the difference between its index of refraction and that of air is much greater, in fact a maximum for white pigments.

Water paints, as the name implies, employ aqueous solutions of a suitable binding agent as vehicle, and although many materials have been employed for this purpose, casein is probably the most satisfactory and widely used. However, glue is also employed to a considerable extent. Pure titanium dioxide and the composites are used in such compositions, but obviously the water-dispersing grades should be selected. As an illustration, a few recommended compositions of this type are described below: A material in powdered form suitable for use as a paint, after mixing with water, consists of 4.25 parts by weight of titanium dioxide pigment, 14 to

45 parts lithopone, 5 to 50 parts barite, 2 to 60 parts whiting, 3 to 25 parts magnesium silicate, 2 to 40 parts china clay, 2 to 15 parts mica, 8 to 15 parts casein, 3 parts Italian talc, borax up to 3 parts and o-phenylphenate up to 3 parts.[15] Jennings[16] employed a mixture of titanium dioxide and silica as pigment, and glue as binder, in a washable wall coating. Still another type consisted of a suspension of 10 parts titanium dioxide, 80 parts magnesium oxide, and 10 parts barium sulfate, in an aqueous solution of magnesium chloride as binder.[17] A paint for wood, paper, stone, or brick consisted of a mixture of titanium dioxide in an aqueous solution of phosphoric acid of specific gravity of 1.2 to 1.3, together with a reversible colloid such as aluminum hydroxide.[18] The pigments set with the acid. A related composition for use on glass or metals consisted of approximately equal parts of aqueous phosphoric acid of specific gravity 1.3 and titanium dioxide of pigment grade.[19]

Unique washable coatings may be produced on walls or other surfaces by first applying aqueous solutions of carboxylated cellulose esters or their soluble salts, such as sodium cellulose glycolate, followed by a titanium salt solution to form an insoluble compound in the film.[20]

Paper

Titanium dioxide, because of its high index of refraction, high brightness, uniformly fine particles, ready dispersion in aqueous media, and good retention in the beater, is widely used in many varieties of paper.[21]

The higher the index of refraction of the filler used, the greater will be the light-scattering property, and consequently the opacity of the system. In an unpigmented sheet the opacity is a function of the difference in the refractive index of the cellulose fibers, and that of the air interspaces, 1.53 and 1.00, respectively. If a mineral filler having a refractive index of approximately the same value as that of the cellulose, such as clay, 1.55, chalk, 1.56, or talc, 1.57, is incorporated, the opacity of the sheet will not be increased appreciably unless large proportions are employed; but on the other hand titanium dioxide with the very high index of refraction of 2.71 would be very effective. Furthermore, if the air spaces in a clay-filled sheet are replaced by another medium as a printing ink vehicle normally having an index of refraction of around 1.50, the difference between this value and that of the fibers and of the filler is so small that the paper becomes translucent or even transparent and the printed characters show through on the reverse side. Here ti-

tanium dioxide is particularly effective, for the difference between its refractive index and that of the ink vehicle is so great that a high degree of opacity is maintained and "show through" is completely eliminated.

In such cases opacity results from the refraction and reflection of light, and the natural white tone and extreme brightness of the titanium pigment are transmitted to the finished sheet. The use of a black dye or pigment would also produce opacity because of absorption of the light, but the resulting paper would be dull and gray.

The average particle size of titanium dioxide is very much smaller than that of the cellulose fibers used for paper making, which average from 10 to 15 microns, so that good adhesion and retention result. Furthermore, the desired degree of opacity is obtained with only a small proportion of titanium dioxide, and the strength, bulk, and sizing of the paper are little affected. Regardless of the amount of rosin, size, and alum used, titanium dioxide does not reduce the sizing resistance to water penetration, as compared with clay or chalk.

As an opacifier this pigment is about ten times as effective as the ordinary mineral fillers, with the result that it is possible to attain degrees which cannot be approached with the older type of agents, and at the same time the color, brightness, and printing surface are much improved. For example, the opacity of a 16-pound rag content bond was increased from 74 to 86 per cent by the presence of 3.8 per cent titanium dioxide, and that of a similar 20-pound unfilled sheet was raised from 82 to 93 per cent by 4 per cent of this pigment. The "show through" was reduced to a great extent, and the color and printing surface were improved. The results of another series of experiments, employing all sulfite paper made under carefully controlled conditions, are shown in Table 20.

TABLE 20
EFFECT OF TITANIUM DIOXIDE ON OPACITY

40-pound *		50-pound		60-pound	
Per cent TiO_2	Per cent Opacity	Per cent TiO_2	Per cent Opacity	Per cent TiO_2	Per cent Opacity
0	75	0	79	0	85
1.3	82	1.3	88	1.3	91
3.0	85	3.0	91	3.0	93
3.6	88	3.9	92	3.9	95

* Basis of weight, 500 sheets, 25 × 38 inches in size.

In 50-pound paper made from a 1 to 1 mixture of bleached sulfite and soda pulp, the superiority of titanium dioxide and composite pigments over clay was clearly demonstrated by actual measurements. (See Table 21.)

TABLE 21

RELATIVE VALUE OF TITANIUM DIOXIDE AND CLAY

	Filler %	Opacity %	Brightness %
None		83.0	82.8
Titanium dioxide (anatase)	3.0	91.4	86.0
Titanium-barium composite (anatase)	6.5	90.0	86.1
Clay	10.0	88.4	84.3

Titanium pigments are relatively inert chemically and are not affected by any of the agents used in making and treating paper; in fact they tend to mask the after-yellowing which normally results from chemical changes occurring in the fibers and sizing on aging.

These pigments have proved adaptable to many paper-making processes. They are widely used as a beater addition, and, although the method varies widely from mill to mill, the most common practice is to add the pigment early in the beating cycle along with the size, while the alum is introduced toward the end to complete the sizing reaction and to fix the pigment on the fibers. Experimental results have demonstrated that an optimum alum addition of around 3 per cent gives best retention, although it will vary, depending upon the type of stock and the operating conditions.

The pigments are finding wide use as a surface application in a great number of methods in which they are applied in conjunction with starch, glue, and similar agents at the size press, in size tubes, at the calender stacks, and by many other specific methods. This treatment markedly improves the printing qualities of the sheet and imparts a much higher opacity and brightness. The casein ratio is about the same as for clay and the method of handling is much the same.

High opacity and absence of "show through" are essential qualities of satisfactory book paper, and with titanium dioxide these properties may be obtained in very thin sheets. Such paper is widely used for printing Bibles, encyclopedias, dictionaries, and one-volume editions of complete literary works and long novels where compactness is desired without the sacrifice of quality. In certain cases,

where higher ash content and thicker sheets are not objectionable, the composite pigments or mixtures of titanium dioxide and clay are frequently employed as beater additions. While a certain degree of opacity may be obtained with the older fillers (clay), their indexes of refraction are so near that of printing ink vehicles that penetration into the paper renders it transparent with the result that the printed characters will show through on the other side. The above statements also hold for all types of magazines and catalogue stock, and to bring out the elaborate illustrations in such publications to the best advantage, paper pigmented with titanium dioxide is employed. Cheap grades of magazines and catalogues are frequently printed on wood sulfite stock, and here the incorporation of titanium dioxide masks the natural yellow color and gives a more pleasing appearance. At the same time it is possible by this treatment to obtain the desired properties in a paper of lighter weight, thus effecting a saving in mailing or shipping charges.

Bond papers opacified in this manner are widely used for printing stock certificates, bonds, insurance policies, and documents of all kinds where good appearance as well as strength and permanence are required. Such paper is also used for advertising booklets, financial prospectuses, and letterheads where excellent appearance is of decided advantage. The better grades of envelopes are made of paper treated with titanium dioxide, and since such small proportions of pigments are required to produce the desired opacity, the natural strength is maintained to a maximum degree. An interesting application is in the various all-purpose papers used for annual reports, booklets, broadsides, calendars, maps, advertising circulars, and letterheads.

Paper or cardboard may be given a brighter, more desirable surface for printing by treatment with a coating composition consisting of titanium dioxide pigment and starch in a solution of a cellulose ether such as alkyl cellulose glycolic acid.[22] Aluminum sulfate can be applied effectively to the coated paper by spraying or immersion. A wide use is in the top liners of boards to prevent the off-colored filler stock from showing through and dulling the surface. Such boards are finding almost universal application in boxes for various purposes, food containers, bottle caps, fiber cans, picnic plates, and show cards. They are especially valuable for packing foods of all types, since the liner will show practically no discoloration in contact with oils, fats, and greases. Paper of this type is also used in making containers for oil.[23] Fiber plates impregnated with titanium dioxide are reported to have been put

through the ovens of a Canadian bakery without excessive loss of strength.[24]

Titanium dioxide pigments are widely used for opacifying, brightening, and whitening tissue paper and to enhance the effect of the printed design. For similar reasons they are employed in glassine, semiglassine, and imitation parchment, which are used not only for wrapping food but also for decorative purposes such as lamp shades and greeting cards. Waxed wrapping paper of extreme thinness can be made with titanium dioxide. These pigments are finding applications in coating colors for paper and boards, and in wall paper.

Cigarette paper [25] of improved quality may be obtained from pulp which has incorporated with it 2 per cent titanium dioxide and 0.8 per cent stearic acid on the dry basis.

Himmell [26] employed titanium dioxide to add underlying imprint markings to paper coated with clay or similar material with relatively low index of refraction. The imprint markings were invisible by reflected light but were quite distinct by transmitted light.

Plechner and Jarmus [27] prepared a stable suspension of titanium dioxide in waxes and resins for coating paper. The pigment particles were intimately mixed with the wax in a softened state in the presence of 0.05 to 0.50 per cent of a metal soap such as aluminum stearate and titanium oleate to effect dispersion; at this stage a small proportion of glycerol, triethanolamine, or its stearic acid ester, cholesterol, lecithin, or boric acid was added to stabilize the suspension and prevent coagulation. Paper impregnated with this composition was impermeable to liquids and gases, and had an opaque finish that remained so in contact with oils and greases. In an actual operation, 150 parts by weight of paraffin was heated to 80° C., and 2 parts of aluminum stearate was thoroughly incorporated into the molten mass, after which 100 parts of titanium dioxide was added. The mixture was then ball-milled at 80° C. for 1 hour to insure thorough dispersion of the pigment, and 3 parts of glycerin was thoroughly incorporated as a stabilizing agent. The cooled product was a pure white homogeneous mass and could be melted and held in a molten state without any appreciable separation of the constituents. A similar thermoplastic suspension [28] was prepared by intimately mixing heat-softened paraffin, gum, or resin with a titanium dioxide pigment and a small proportion of a lipoid such as cholesterol or lecithin. Ball [29] prepared a composition for coating paper or cloth by incorporating a titanium pigment in a mineral wax with the aid of a dispersing agent such as sulfonated oil.

The product was applied while in the molten state. Paper coated with a flexible, opaque, moisture-resistant composition formed of paraffin 100 parts, carrying in colloidal solution 1 to 3 parts of rubber or polymerized isobutylene, 5 parts titanium dioxide for each part of rubber, and sodium benzoate in a quantity not exceeding that of the rubber, proved well suited for wrapping bread, cakes, and other articles of food.[30]

From optical measurements, Hansen [31] showed the superiority of titanium dioxide over other agents in brightening and opacifying waxed paper.

Frost [32] applied a surface coating of an aqueous dispersion of an adhesive with titanium dioxide and chalk to paper, dried the composition, smoothed and leveled the surface by calendering, and applied a film of clear lacquer to obtain a high finish.

Textiles

DELUSTRANT. Rayon produced in the early days of the industry had a high luster which for many purposes was objectionable and readily distinguished it from real silk. Many procedures and materials have been employed to overcome this undesirable feature, and these may be divided into two groups: those in which the delustering agent is added to the viscose or other solution prior to coagulation, and others in which the agent is added, or applied as an after treatment, to the yarn or fabric. These methods are usually referred to as "internal" and "external" delustering, respectively, and each offers certain advantages and disadvantages. In the first a matte effect resistant to washing and exhibiting a certain degree of permanency is obtained, while the other method permits a wider degree of delustering and is capable of meeting particular requirements. By the external process the material may be delustered before or after dyeing.

Water-white paraffin dispersed throughout the viscose was found to give a satisfactory matte effect combined with a soft handle, but this operation failed to produce the very dull finish later demanded, so the use of insoluble pigments followed. It is in this field that titanium dioxide has proved to be of such great value, and the pigment has found extensive application in delustering artificial fibers.[33]

Light falling upon a fiber will be specularly and diffusely reflected to varying degrees, depending upon its physical properties. In the case of a smooth untreated thread, most of the light will be

specularly reflected, that is, it will leave the surface at an angle equal to the angle of incidence and the rayon will appear shiny. If a pigment is dispersed throughout the fiber, however, as for example by coagulation of a spinning solution in which such particles are dispersed, part of the light will be reflected at the surface and the remainder will be refracted into the interior. As a result of the two-phase system, a number of reflecting interfaces are introduced into the body of the fiber and these yield a large proportion of diffusely reflected or scattered light. It is in this respect that a difference as large as possible should exist between the refractive index of the delustrant and that of the cellulosic material of the rayon; that is, the reflecting efficiency of the pigment interfaces depends upon this factor, together with particle size and the percentage present. The light after multiple reflection and refraction emerges from the fiber, but at an angle not equal to the initial angle of incidence, and thus produces a dull or matte appearance. While in the lustrous yarn regular reflection occurs, with the optically heterogeneous fiber reflection from the surface is in all directions, and light is diffusely reflected. Thus the most efficient agents for producing the matte effect in synthetic fibers are pigments having high indices of refraction, such as titanium dioxide, so that there is a wide difference between the refractive index of the added agent and that of the cellulose or other material making up the fibers of the textile. The amount of light reflected at the interfaces is therefore maintained at a maximum.

Pigments for this purpose must be capable of fine subdivision and high dispersion. The degree of reflection for a given system increases with increasing fineness of the agent to a diameter equal to the wave length of visible light. If the particle size is reduced below this value, the incident light will not be reflected, but an interference effect will result and part of it will pass the solid particles. Furthermore, the delustrant must not have a detrimental effect upon the strength of the fiber, dyeing properties, and handle, and must be inactive chemically. For example, in viscose the agent employed must be resistant to the severe acid and alkaline conditions existing throughout the spinning phase of the process, as well as to the chemicals used throughout the after-treatment of the threads or cloth.

Titanium dioxide fulfills these requirements to a higher degree than any other available material, and is used extensively in producing the extremely dull rayons so much in demand at the present time. Properties which make this pigment especially effective for

the delustering of viscose are high index of refraction, low specific gravity, fine particle size, and chemical stability. It is insoluble in acids and alkalies; it is unaffected by heat; it does not discolor on aging or on exposure to sulfur gases; and it is not toxic. The latter property is particularly important in the manufacture of rayon for clothing and household articles.

One disadvantage is the increased wear on the manufacturing equipment resulting from the abrasive effect of the added pigment, and the possibility of blocking and roughening the outlets from the spinneret faces. In producing delustered yarns, the surfaces of the guides are worn into grooves more rapidly by the pigment particles of the moving filament, and the grooves thus formed may cause damage to the freshly formed thread. Such difficulties are more than counterbalanced, however, by the inherent advantages of the titanium dioxide, and they may be minimized by employing the softer grades of pigment that has not been overcalcined, and the more effective methods of dispersing the solid particles in the viscose liquor. Thus, so far as the spinning is concerned, it is important to avoid pigment having extreme hardness and oversized particles.

Titanium dioxide may be incorporated into the individual fibers most effectively by dispersing the finely divided and uniform pigment in the ripened viscose, and it is held in the mass of the cellulose after coagulation into threads. Any oversize particles should be removed, since they would remain in the viscose and result in loss of strength of the fibers and tend to block the openings of the spinnerets. This may be accomplished prior to spinning by a number of processes, such as filtering through a medium of proper-sized openings, by centrifugal separation, and by elutriation.

By the external method of delustering, particles of titanium dioxide are precipitated on the surface of the formed fibers from a stabilized dispersion of the finely divided pigment by adding a coagulating agent (electrolyte) or from solutions of titanium salts, such as sulfate or chloride, by hydrolysis, or by adding an alkali (ammonium hydroxide). In this method the index of refraction of the pigment with reference to that of the fiber material is no longer of such great importance as the main reflecting surfaces are in contact with air. To produce a satisfactory degree of permanency, however, the particles of the precipitated agent must be small enough to fit securely into the striations of the fiber, and if this is accomplished the finish will be reasonably stable to washing and the product will have a good handle. Physical properties of the precipitates are controlled largely by the concentration of the liquor

used, and the ratio of titanium dioxide to sulfuric acid in the solution has a considerable effect upon the opacity of the final product. Titanium dioxide in a hydrous condition may be successfully employed as an external delustrant, although it has a much lower index of refraction than the calcined product.

Obviously the increased wear and tear on the plant resulting from the pigment particles can be avoided by delaying the treatment until just before or after dyeing. The method also reduces the difficulties associated with mixing and filtering the viscose, and a plant designed for producing shiny rayon may turn out the dull grade simply by installing the extra step of precipitating the pigment on the coagulated filament without installing new equipment or involving complications in the mixing, ripening, and spinning steps.

Many patents dealing with the various phases of delustering rayon have been issued, and a few representatives are outlined here to illustrate the general method. Raspe and Giese [34] dispersed finely divided, acid-free, precipitated titanium dioxide, which had been dried but not calcined, in viscose solutions in proportions of 1 to 5 per cent of the cellulose content, and coagulated the suspension to produce fibers of dull luster. In a similar procedure, hydrous titanium oxide was dried by contact with hot vapors of organic substances, such as anthracene and olive oil, before incorporation in the viscose solution.[35] Pigments treated in this manner were also applied to the finished thread by coagulation from suspension. A homogeneous spinning suspension was obtained by introducing into 10 liters viscose solution containing 7.8 per cent cellulose and 6.5 per cent sodium hydroxide, while agitating, 15 to 30 g. of a composition formed by grinding together 70 parts titanium dioxide and 30 parts of the sodium salt of the condensation product of beta naphthalenesulfonic acid with formaldehyde.[36] Nijma [37] added 2 per cent titanium dioxide to ground and ripened alkali cellulose and kneaded the mixture with carbon disulfide to insure thorough mixing.

Titanium dioxide pigments were suspended in the reactant mixture used for the preparation of cellulose esters and precipitated along with the ester.[38] Such products were used alone or mixed with the unpigmented material for the preparation of yarns or films having a matte effect. Delustered fibers, films, ribbons, or bristles were produced from superpolyamides, polydecamethyleneadipanide (nylon), by incorporating finely divided titanium dioxide in the plastic before spinning or drawing.[39] These compositions could be cold drawn.

Cremer [40] treated rayon or mixed fabrics with a dispersion of titanium dioxide stabilized with lecithin and a mono- or poly-hydric lower alcohol, and coagulated the pigment on the threads to produce a dull appearance. Craik [41] impregnated lustrous products from viscose or cellulose acetate with a dispersion of finely divided titanium dioxide in a caustic alkali solution of a low substituted cellulose derivative such as methyl or ethyl cellulose, and neutralized the alkaline material to effect precipitation of the pigment on the rayon material to remove the high luster. The low substituted cellulose should be incompletely soluble at room temperature, but completely soluble below 10° C. A similar effect was produced by wetting the rayon material with a solution of titanium ammonium tartrate and heating it with moist steam containing ammonia, for 10 minutes, to precipitate titanic oxide on the fibers. [42] According to a closely related process, cellulose acetate fabric was passed through an aqueous 20 per cent solution of titanic chloride at such a rate that it picked up an equal weight of the tetrachloride and was later passed through an atmosphere of steam and ammonia at approximately 100° C. for 2 minutes. [43] Titanium dioxide was thus precipitated, giving the cloth a delustered appearance. The dullers generally used for producing chalk-finish bengaline are mixtures of inorganic compounds, e.g., titanium dioxide and aluminum silicate. [44]

The dyeing of rayon delustered with titanium dioxide is by no means free from difficulties, and it has been observed that fading of the applied dye on exposure to light may be accelerated by the pigment, particularly while wet. [45] Such yarns, treated with glycerin in any phase of their processing, were especially subject to fading. According to Ellis and Stanley, [46] this undesirable property was counteracted by incorporating in the composition compounds of vanadium, tantalum, and related elements; copper compounds were also effective. In a specific example, finely divided titanium dioxide was heated to 85° to 90° C. with an aqueous solution of ammonium vanadate and formic acid, the coated particles were filtered, washed, and dried, and incorporated in a cellulose acetate spinning solution. The method proved applicable to textile materials, films, and molded articles. Mudford [47] mixed pigment for this use with an inorganic compound containing as its sole amphoteric metal constituent an element of Subgroup A, Group VI of the Periodic Table, such as sodium chromate, sodium tungstate, and sodium molybdate, to improve its resistance to fading of dyes. Titanium dioxide, treated with copper sulfate or similar compounds of manganese, iron, cobalt, or nickel, imparted improved light fastness to cellulose

acetate compositions such as those used for making filaments, films, and molded articles.[48] Dyed rayon, pigmented with titanium dioxide previously treated with an insoluble fatty acid salt of high molecular weight (at least 8 carbon atoms), showed improved fastness to light.[49] In an example, cloth dyed with orange Congo G was treated with a suspension of 100 kg. titanium dioxide in 100 kg. of an 8 per cent solution of aluminum stearate in carbon tetrachloride.

FABRIC PRINTING. Cotton fabric may be ornamented by applying a thickened aqueous solution of methylolurea pigmented with titanium dioxide, followed by drying and parchmentizing in the usual manner.[50] The latter treatment fixes the thickener so that the cloth has the same degree of thickness in the printed and unprinted portions. In a particular application, a printing paste containing titanium dioxide 30, dimethylolurea 14, gum arabic 20, sodium formaldehydesulfoxylate 5, and water 31 parts was printed on a well mercerized cotton lawn previously dyed pink with Chorazol fast red K. The fabric was dried, steamed 5 minutes to discharge the pink ground under the printed parts, treated without tension in an 88 per cent solution of phosphoric acid containing 0.5 per cent formaldehyde for 30 seconds at 50° C., washed free from acid, and dried. A soft waterproofing ingredient made of egg white or gelatinous substance, Japanese wax, castor oil, olive oil, or metal soap of oleic acid, mixed with titanium dioxide pigment and a soluble dye, was employed as printing paste.[51] The cloth printed with this composition was steamed and dried.

Titanium dioxide has also been used in lacquers and other compositions for printing designs on fabrics.[52] In an example, a mercerized muslin was printed with a gum reserve and parchmentized by heating it with sulfuric acid. A partially overlapping pattern was then printed with another reserve consisting of chlorinated rubber, toluene, pine oil, and titanium dioxide pigment, and the cloth was shrunk in an alkaline bath.

STIFFENING AND BRIGHTENING FABRICS. Other applications are in thermoplastic adhesives [53] used for stiffening fabrics. Layers of cotton or linen cloth, united and stiffened with a thermoplastic cellulose derivative such as the acetate, were treated with a titanium dioxide composition to improve the whiteness and brightness.[54] Laminated materials of this type were used in making collars and cuffs. The brightness of the finish of white linen, cotton, and other fabrics was improved by using a starching composition con-

taining titanium dioxide.[55] This treatment was applicable to laundered goods as well as to new fabrics.

Rubber

Because of its unequaled opacity among white pigments, high total reflectance, and small particle size, titanium dioxide is particularly well suited for producing white and light-colored rubber goods. An exact table of relative tinting strengths of pigments in rubber compositions is difficult to set up, since the type and color of the testing formulas and variations in laboratory procedures affect the results. The approximated values shown in Table 22, however, make clear the great superiority of titanium dioxide in this field.

TABLE 22

RELATIVE TINTING STRENGTH OF WHITE PIGMENTS IN RUBBER
COMPOSITIONS

Pigment	Equivalent Parts by Weight
Titanium dioxide (rutile)	0.75
Titanium dioxide (anatase)	1.00
Zinc sulfide	2.2
Titanium dioxide-calcium sulfate (rutile)	2.3
Titanium dioxide-calcium sulfate (anatase)	3.0
Titanium dioxide-magnesium silicate (anatase)	3.0
High-strength lithopone	3.0
Titanium dioxide-barium sulfate (anatase)	3.5
Regular lithopone	5.2

Thus a high degree of whitening may be obtained with a minimum amount of pigmentation, with the result that the desirable natural properties of the rubber can be maintained to the highest degree.

Titanium dioxide does not function as an activator in hot methods of curing which employ organic accelerators, and a small proportion of zinc oxide is included in the charge for this purpose. Because of its strong plasticizing effect, the rate of vulcanization is retarded slightly. Rubber stocks compounded with titanium pigments have good aging characteristics, high tensile strength and elongation, and excellent resistance to discoloration by sunlight. The abrasion, flexing and tear resistance, resilience, hardness, and modulus of cured titanium dioxide pigmented rubber are equal or slightly superior to those of similar products containing an equiva-

lent amount of zinc oxide. Titanium dioxide has been reported to soften rubber notably during milling, but the choice of accelerators that will produce a strictly white vulcanite with it as the only white pigment is limited.[56]

According to Ditmar,[57] the time for curing rubber mixtures either by sulfur chloride vapor or by dipping in solutions of this agent in carbon disulfide is slightly increased by the presence of titanium dioxide, but the products are of an excellent white color and are more supple. In curing by hot methods with organic accelerators, titanium dioxide is a substitute for zinc oxide as an activator, but because of its strong plasticizing effect it slightly retards the rate of vulcanization. Because of this property, titanium dioxide in the proper proportions may prevent "scorching" of the rubber mixture during curing. It confers a greater water resistance [58] on the vulcanite than zinc oxide. According to Saito and Isiguro,[59] aging of rubber pigmented with titanium dioxide, zinc oxide, and lithopone showed no appreciable difference. Gardner [60] found that rubber compositions pigmented with 30 per cent or more titanium phthalate showed improved stability on exposure to ultraviolet light.

Scott [61] found that titanium dioxide showed in vulcanized rubber stock 2 to $2\frac{1}{2}$ times the pigmentary power of zinc sulfide, 5 times that of lithopone, and 12 times that of zinc oxide. Composite pigments showed pigmentary properties roughly proportional to their titanium dioxide content. The relative tinting strengths of all the types of titanium dioxide pigments were in approximate agreement with the values calculated from their average index of refraction. Commercial lead titanate was found to be unsatisfactory for rubber because the traces of free lead oxide which it contained reacted with sulfur in the vulcanization process.[62] The dioxide had an accelerating effect on vulcanization and increased the tensile strength and rigidity, but had a detrimental effect upon aging properties. Dorey and Scott [63] reported that titanium pigments had a slightly accelerating action on rubber-sulfur mixtures, and that such products aged as well as those containing zinc oxide or lithopone. The superior whitening power of titanium dioxide was maintained during accelerated aging. Reports of valuable reinforcing properties of the titanium dioxide pigments were not supported.

Pure titanium dioxide and the calcium sulfate base composite are the grades generally preferred in rubber compounding, and the former is used in compositions requiring the greatest pigmentary value with a minimum of loading. These pigments are used in

soft and hard rubber compositions with light and heavy loading. Specific applications are in the manufacture of white-walled automobile tires, white and tinted rubber sheets and fabrics, rubber shoes and bathing suits and caps, household articles, hospital goods, toys, golf and tennis balls, and many molded articles of hard rubber.

Titanium dioxide has also been used in pigmenting plastic masses from rubber latex,[64] and has been added to chlorinated rubber during milling to retard decomposition under heat and mechanical treatment.[65]

Plastics

According to Wait and Weber,[66] titanium dioxide is used as an opacifying and whitening agent in almost every variety of plastic material and molding powder except urea and thiourea mixtures. It is particularly applicable in cellulose nitrate, cellulose acetate, and viscose compositions, and in white and tinted casein plastics. Plastics of the celluloid type are often treated after polishing with acetic acid, and here the chemical inertness of titanium dioxide is important. Zinc oxide, for example, would be attacked, thus damaging the surface of the article. Casein usually contains residual lactic acid so that it cannot be mixed with reactive zinc oxide and lithopone, and such pigments do not produce the desired whiteness. Here again, because of its high opacity and chemical inertness, titanium dioxide gives a very white and opaque product.[67]

These pigments have been added to the relatively dark phenolformaldehyde molding powders to lighten the shade, have been incorporated with styrene and polymerized methylmethacrylate plastic compositions for making dentures,[68] and have been used for pigmenting melamine laminates,[69] and silicone resin coating compositions.[70] The backs of adhesive sheets have been coated with a plastic composition consisting of cellulose nitrate, titanium dioxide pigment, and a plasticizer.[71]

Ellis [72] reported a number of applications of these pigments in various types of synthetic resins. A molding composition was produced from a mixture of 40 parts polymerized vinyl chloride, 10 parts alkyd resin, 30 parts dibutyl phthalate, 7.5 parts alpha cellulose, and 12.5 parts titanium dioxide pigment. The polymerization of a mixture of vinyl chloride with less than 43 per cent vinyl acetate, in the presence of titanium dioxide, yielded a uniform moldable resin recommended for sound records and floor and wall surfaces. It was also incorporated into vinyl resin compositions for molding into sound records to increase the hardness and active

life of the products. Titanium oxide has been applied, along with water soluble urea-formaldehyde resins, to cotton and rayon fabrics to render them less susceptible to creasing and wrinkling without at the same time adversely affecting their suppleness. An insulation for copper wire consisted of a coating of titanium dioxide in a phenol-formaldehyde resin binder. Other applications are in the production of white and light-colored floor coverings (linoleum), oilcloth, and artificial leather.

Senac [73] gave an outline of the methods for physical and chemical examination of titanium pigments from the standpoint of determining their suitability in plastic compositions.

Printing Inks

One of the first commercial uses of titanium dioxide pigment was in inks, and because of special properties, application in this field was economically practical even at prices that excluded it from the paint industry. In this connection the most important characteristics are high opacity in oil or resin vehicles, chemical inactivity, fine particle size, and resistance to discoloration on exposure to heat and light.

The inertness of titanium dioxide permits formulation in a wide variety of varnish vehicles, regardless of their acidity, without danger of livering. This factor, however, introduces other problems in connection with the physical properties of the ink. For example, its ease of wetting and degree of dispersion are largely determined by specific vehicle characteristics, exclusive of chemical reaction. Wetting is dependent upon the relative polarity of the vehicle, so that acidic compounds, developed as a result of heating, will exert a beneficial effect on the wetting and dispersing properties. If the acid number of the varnish is for other reasons fixed at a low value or the nature of the oil is such that acidity does not develop on processing (tung oil), these characteristics may be improved by incorporating fatty acids or their metallic salts (soaps) in the vehicle before mixing and grinding. Examples of effective agents are zinc oleate, zinc naphthenate, sulfonated oils, ester gum, and the reaction product of litharge with the oil at cooking temperatures.

In general, the ease of dispersion varies inversely as the oil grades contain larger and more compact aggregates. Thus if it is possible to sacrifice some hiding power as a result of reduced pigment concentration, increased dispersion may be effected by employing a product of medium oil absorption.

All titanium dioxide of pigment grade is of the same order of hardness, since maximum opacity is obtained only with the development of definite crystal structure. Since both opacity and hardness are functions of the crystal form, there can be no real difference in hardness between different lots having the same degree of opacity, but the abrasive action may vary widely. Titanium dioxide is never dispersed in inks or paints to the ultimate particles, but always in the form of aggregates or groups of individual units, and as the size increases there will be a corresponding increase in abrasive action. For this reason wetting and dispersion of the pigment becomes important.[74]

As a result of the extremely small particle size, inks containing high percentages of titanium dioxide are characterized by exceptionally dense, nonrubbing qualities. Even at a magnification of 100 diameters the individual particles cannot be detected, and the ink film appears to be perfectly homogeneous.[75]

Titanium pigments are widely used in lithographic and metal decorating inks, and results may be obtained with a single impression that formerly required two or more. They are of particular value in producing various tints with a minimum amount of pigmentation so as to bring out especially strong and clear colors. Other applications are in the production of opaque tint bases and cover glassine tin-printing and decalcomania whites. The special antimony-trioxide-containing grade may be used in offset printing inks without danger of bleeding. In this process the plates are washed between impressions with dilute aqueous phosphoric acid, which has a strong tendency to produce smearing of the inks containing the regular-grade pigment. A nonbleeding printing ink of this type may be formed with an oleaginous vehicle pigmented with titanium dioxide calcined with a small proportion (around 1 per cent) of antimony trioxide, or a compound that will yield this oxide, and subsequently coated with hydrous aluminum oxide.[76] The latter is best applied by chemical precipitation of the alumina on the finely ground titanium dioxide particles suspended in an aqueous medium. Such a pigment, stable and resistant toward lithographic breakdown, may be produced by precipitation on the surface of the particles (subsequent to calcination) from 0.2 to 2 per cent of hydrous titanic oxide.[77] After treatment, the pigment is dried at a temperature not exceeding 200° C. To produce a lighter shade of a particular color of printing ink, Wood[78] employed a translucent extender consisting of hydrous oxide of titanium, zirconium, or silicon.

Cosmetics

Titanium dioxide pigments have many applications in cosmetics. All types of powders have certain properties in common, the most important of which are covering power, slip, adhesiveness, and absorbency. Because of its high opacity titanium dioxide has almost completely replaced zinc oxide as the hiding component. The desired permanent whiteness can be obtained and maintained in use with only 5 to 8 per cent of this pigment, with the result that larger proportions of the other constituents may be employed, thus imparting their specific properties, as, for example, slip and adhesiveness, to the maximum degree. In high proportions titanium dioxide would produce too great opacity and tend to give the skin a coated chalky appearance. The pigment is also used in liquid face powders and in vanishing and cold creams to overcome the waxy, translucent appearance and impart the highly desirable properties of color and opacity. For this purpose less than 5 per cent is usually sufficient.

It is employed to a considerable extent in the preparation of skin lotions, and is an effective pigment for perspiration and water resistant sunburn protective lotions and creams.[79] In sunburn lotions it has the advantage of actually deflecting the sun's rays. The pigment is added to soap flakes, white toilet soap, and shaving soaps and cream in proportions of around 1 per cent to prevent excessive translucency, to overcome the natural waxy appearance, to impart whiteness, solidity, and opacity, to mask yellowing, and to improve the general appearance of the product.[80] If a creamy translucency is desired, the amount of the agent may be decreased to 0.25 to 0.50 per cent. The titanium dioxide may be incorporated in the soap stock as a suspension in water or glycerin. Other applications are in various waxes, nail polishes, nail whiteners, and depilatories; as a constituent of cosmetics for photographic make up; in grease paints, in wet white, and in white tooth enamels. Creams containing titanium dioxide are less liable to impart an oily or greasy appearance to the skin. It has been recommended as a polishing agent for tooth powders and pastes.

Miscellaneous

Cellulose fibers or fabrics can be rendered resistant to fire, water, and mildew by applying a single coating of a composition containing 15 to 30 per cent chlorinated paraffins, 5 to 15 per cent zinc borate,

titanium dioxide as whitening agent, china clay as loading agent, and triphenyl phosphate as plasticizer.[81] A fireproof composition for paints and glues contained parts by weight titanium dioxide 150, zinc oxide 407, linseed oil 170, stand oil 70, turpentine oil 20, manganese resin 90, barium sulfate 36, silica and calcium silicates 2.2, zinc sulfide 15.5, iron oxides 1.4, alumina 2.1, magnesium oxide 2.6, and calcium carbonate 32.3.[82] Similar compositions may be employed for fireproofing buildings.[83] A marking implement [84] has been made from a composition containing titanium dioxide, rosin, linseed oil, and a drying accelerator. The film formed on exposing the mixture to air maintained the inner portion of the stick in an unhardened condition. In preparing record material for typewriters and autographic registers, a sheet of dark paper was coated with a thermoplastic layer consisting of a synthetic resin (polyvinal acetate), a solvent (ethyl acetate), and titanium dioxide of pigment grade.[85]

A skin-sealing composition for morticians' use was composed of amorphous rubber hydrochloride 100 parts, hexamethylene tetramine 2 parts, titanium dioxide 2 parts, magnesium oxide 30 parts, and a red dye dispersed in a volatile solvent so that the product contained 15 per cent solids.[86]

Allen [87] covered the surface of coal with a uniform coating of titanium dioxide in a casein vehicle to impart a white appearance. The application also reduced atmospheric deterioration, made the product clean and dustless, and on ignition controlled the burning characteristics of the coal so as to prevent formation of smoke and soot. With proper modifications run-of-mine coal was simultaneously washed and coated.[88] The crude material was dumped into a suspension of titanium dioxide, a glue-like binder, and a dispersing agent in a volatile medium of such proportions that the resulting fluid mass had a specific gravity higher than that of pure coal but lower than that of the gangue material. After thorough agitation (jigging), the segregated layer of pure coated coal was removed from the bath and dried.

Coated metal for reflectors was prepared by applying multiple layers of titanium dioxide in water glass.[89] Each application was dried before another was added. Titanium pigments have been incorporated into asbestos composition shingles and building boards to improve the whiteness and brightness, and they have been used to whiten cements and produce special finishes.

Chapter 21

IRON AND STEEL

Ferroalloys

Alloys of titanium with iron, particularly ferrocarbontitanium, are important in metallurgy, and these are consumed in steadily increasing quantities not only in steelmaking but in producing iron castings and various nonferrous alloys. Formerly used almost exclusively as a deoxidizer, it has assumed considerable importance in the manufacture of stainless steels to inhibit intergranular corrosion. The use of ferrotitanium alloys in making steel for deep stamping, for automobile body stock, and for tinned and galvanized roll sheets has increased greatly. In the production of intermediate manganese steels, ferrocarbontitanium is replacing more expensive agents, notably nickel and vanadium. Other important developments have been in gray cast iron, in the temper-hardening of copper-titanium alloys, and in aluminum. It has an important application in making various castings and forgings, including chilled iron car wheels and machine parts.

Rossi, a young French metallurgist, came to the United States in 1870 to engage in the blast-furnace smelting of titaniferous iron ores. As an outgrowth of this work he developed the first economical process for making high titanium alloys, and by 1895 he had produced both ferrocarbontitanium and ferrotitanium in the electric furnace.[1] In the manufacture of ferrocarbontitanium, ilmenite, scrap iron, and coke were mixed together in the proper proportions and charged into an electric furnace of special design. The current was so regulated as to maintain a temperature of 2000° C.[2] As soon as the reaction had proceeded to completion, the molten mass was tapped at the bottom vent and run into molds. The very small amount of slag obtained was returned to the furnace with a later charge. After cooling to room temperature, the alloy was broken, crushed, screened, and sold in different sizes, according to the purpose for which it was intended.

The construction of the furnace departed from the conventional practice in that it had only one electrode. This was connected to the

positive side of the line and could be moved up and down to adjust the amount of current flowing through the charge. The other electrical contact was through the graphite lining of the hearth and part of the walls of the furnace. For the remainder of the lining, a nonconducting refractory material was employed.

Similar products were obtained by reducing a titaniferous iron ore in an electric furnace at 500 amperes and 50 to 60 volts.[3] A typical charge consisted of 100 parts of the ore containing 67 per cent ferric oxide and 14.5 per cent titanium dioxide, 16 parts limestone, and 30 parts of carbon as coke. According to a modified process, a charge containing titanium ore and a carbonaceous reducing agent was smelted in a carbon-lined electric furnace in the presence of a refractory material composed primarily of an oxide of zirconium or beryllium, thereby providing a working bottom or interlining and lowering the carbon content of the product.[4] Manganese and silicon were also added to raise the titanium content of the alloy. The melt was tapped intermittently. In a similar method, oxides of aluminum or magnesium were added to the charge, instead of oxides of zirconium or beryllium.[5] Alloys of titanium and any miscible metal, such as iron, chromium, and manganese, may be produced by smelting an intimate mixture of titanium dioxide, carbonaceous reducing agent, products rich in alumina, silica limestone, or fluorite, and ore of the desired metal in the electric furnace.[6]

Horneman [7] reported a process for producing ferroalloys of titanium in the blast furnace. A charge of iron ore, flux, and coke was smelted in the usual manner, and the slag was drawn off, leaving the molten metal in the furnace. A secondary charge of titanium ore and coke was then introduced, and the furnace was operated to produce elemental titanium which went into the iron. Slag formed in this stage was separated and the alloy was drawn off into casting molds.

Mayer and Gredt [8] first made briquettes of the titanium ore (ilmenite), with the necessary carbon for reduction, employing powdered iron or ferrous oxide and an oxidizing agent as the bonding material. By its initial oxidation the iron formed an agglomerating agent and cemented the constituents into a solid porous form. The briquettes were then reduced to form an alloy of iron and titanium.

Ferrotitanium containing practically no carbon was made by an electric-furnace method in which the reduction was brought about by a bath of molten aluminum.[9] Metallic aluminum was first charged into the furnace, and the electric current was turned on until it was

completely liquefied. Oxide ores of titanium and iron or scrap metal were then introduced into the molten aluminum, and the current was introduced, if necessary, to raise the temperature of the charge to the point at which the reaction commenced. In general, the current could be turned off as the exothermic reaction proceeded, but at any rate the temperature of 2000° C. required for the process was maintained. After the reduction had gone to completion, the slag was withdrawn through the upper outlet and the molten alloy was tapped at the bottom of the furnace. As a rule, oxide ores were charged in proportions equivalent to the aluminum present, but one of the advantages was the facility with which any residual aluminum could be removed from the metallic product merely by the addition of more of the ores to the molten mass. The oxide to be reduced was introduced into the bath gradually, in successive charges, instead of all at once.

Ferrotitanium practically free from carbon was produced by the aluminothermic process of Goldschmidt.[10] An intimate mixture of iron oxide, titanium oxide, and metallic aluminum, all in the form of fine powders, was placed in a refractory vessel, and by means of a fuse some point within the mass was raised to the ignition temperature. Once initiated, the reaction between aluminum and the combined oxygen of the ores spread almost instantaneously to the entire mixture, with the evolution of much heat and light. To get the reaction started vigorously, the fuse of magnesium ribbon, where it extended into the mix, was usually surrounded with a priming charge consisting of aluminum powder and barium peroxide. Alloys of this type containing higher percentages of titanium were successfully employed in treating iron and steel, as the aluminum content was said to facilitate solution of the titanium in the molten metal with the result that the action took place much more quickly. In practice, best results were obtained with alloys containing around 25 per cent titanium and 3 per cent aluminum. One of the principal advantages resulting from the addition of aluminum was that the melting point of the alloy was lowered and at the same time its activity was considerably increased.

Mathesius [11] produced ferrotitanium by the aluminothermic reaction of a mixture of ilmenite, aluminum, and a metal oxide richer in oxygen than ferric oxide, for example, manganese dioxide. Alloys made in this manner were readily taken up by molten iron or steel if added in the fused state. At the Chusov plant [12] (U.S.S.R.) the alloy was produced by reducing ilmenite concentrates with aluminum, after the method of Goldschmidt. Yields of titanium ranged from 50 to 60 per cent, and the product analyzed 18 to 25 per cent tita-

TABLE 23

TITANIUM ALLOYS USED IN STEELMAKING

Constituents	Original or High-carbon Ferrocarbon-titanium (Per cent)	Medium-carbon Ferrocarbon-titanium (Per cent)	Foundry Ferro-titanium (Per cent)	Low-carbon 40 per cent Ferro-titanium, Regular (Per cent)	Low-carbon 40 per cent Ferro-titanium, Low Aluminum (Per cent)	High-aluminum Ferrocarbon-titanium (Per cent)	Manganese Titanium, Regular (Per cent)	Nickel Titanium, Regular (Per cent)
Titanium	15-18	17-20	18-23	38-42	38-42	12-17	25-28	25-28
Total carbon	6-8	3-5	0-0.5	0-0.5	0-0.1	2-5	0-0.1	0-0.1
Graphite	3-4	0-0.1						
Silicon	2-3	2-3	18-23	3-5	9-13	2-3	2-4	1-3
Aluminum	1-2	1-2	0-1	6-9	2-5	17-22	7-9	6-8
Manganese	0-1	0-1	0-1				35-40	
Iron	70	70	57	47	45	55	20-25	2-5
Sulfur	0-0.1	0-0.1	0.01					
Phosphorus	0-0.1	0-0.1	0.01					
Nickel								50.6

nium, 0.15 per cent carbon, aluminum up to 5 per cent, phosphorus 0.08, and sulfur 0.10 per cent. The method of Rossi was reported to give poorer yields, 38 to 50 per cent.

Ferrotitanium can be rolled, and may be used as alloy steel.[13] With high titanium content, the products were susceptible to aging, and the grain structure was very coarse. From a study of the penetration of titanium into iron, nickel, and copper, Kase [14] found that diffusion began at 800° C., and that the rate increased as the temperature rose to 1300° C., the limit of the range investigated. Although the cemented surface was harder than the base metal, there was only a slight increase in resistance to corrosion.

The carbureted alloy is less expensive to produce, and for practically all purposes the carbon content is not objectionable. As a result, the pioneer producer, Titanium Alloy Manufacturing Company, with electric-furnace plants at Niagara Falls, New York, specializes in this material and produces smaller amounts of the low-carbon and carbon-free grades. The first commercial production was in 1906. The Vanadium Corporation of America makes the ferro-carbontitanium alloy at the Niagara Falls, New York, plant, and the low-carbon grades at Bridgeville, Pennsylvania. Ferrotitanium is also produced by the Metal and Thermit Corporation at its Carteret, New Jersey, plant.[15]

Various grades of ferrotitanium alloys used in steelmaking, together with representative analyses,[16] are given in Table 23.

Smelting Titaniferous Iron Ores

The commercial utilization of titaniferous iron ores in the blast furnace has been the subject of much controversy, but it seems to be generally held that such ores cannot be smelted economically, particularly if they contain an appreciable proportion of this element. However, Rossi, who devoted much of his time for over thirty years to investigations of ores of this type and processes for their utilization, disagreed with this view, and in support thereof cited the blast furnaces that operated on such ores on a commercial scale in Sweden, Norton-on-Tee, England, in the Adirondack region of New York, and at Boonton, New Jersey. His work indicated that with proper fluxing and with suitable conditions of temperature and blast pressure, these ores could be smelted successfully to yield iron of excellent quality, although these results were obtained in the older furnaces operated at not too high temperature so that practically all the titanium of the charge went into the slag. With the modern

furnaces, employing higher blast pressures and temperatures, products that were fusible with difficulty and that had a metallic appearance and properties such as the nitride or cyanonitride would probably form and, if excessive, would tend to give trouble. Of possible significance is the fact that the extensive deposits of titaniferous iron ores in the Adirondack Mountains of New York had not been used for many years prior to the war emergency of 1941.

Iron ores containing 9.31 per cent titanium dioxide have been smelted successfully in New Zealand.[17] Approximately 85 per cent of the titanium in the charge went into the slag, 5 per cent into the cinder, and 10 per cent was reduced to the metal and alloyed with the iron. Actual practice indicated 0.6 per cent as the average value at which absorption ceased. However, cast iron containing more than 0.6 per cent titanium was produced in the blast furnace by holding the temperature above 1600° to 1800° C., and by employing a slag composed primarily of aluminum silicate, which reduced titanium oxide to the metal.[18] A typical fusion bed contained 3 parts bauxite, 0.3 part ilmenite, 3.75 parts scrap iron, and 3 parts limestone. A number of references to the blast-furnace smelting of titaniferous magnetites in the Union of Soviet Socialist Republics have appeared in the literature in recent years,[19] and slags containing from 5 to 37 per cent titanium dioxide were said to have been handled successfully. The difficulties normally encountered in smelting such ores were overcome by replacing a part of the calcium oxide of the charge with sodium chloride.[20] To insure better mixing and retention, rock salt was added to the coal before coking and incorporated in this manner. In a laboratory blast furnace all the titanium dioxide of the charge went into the slag, which contained 43 per cent of this constituent and 5 per cent sodium chloride.

The German steel industry developed emergency methods for successfully smelting titaniferous ores in the blast furnace without increase in coke consumption and without trouble in slag control.[21]

Although titaniferous ores in a number of instances have been smelted in the blast furnace, Stansfield[22] concluded that the titanium dioxide content must be below 1.5 per cent in making foundry iron, and below 3 per cent for the malleable variety. By magnetic separation the titanium dioxide content of Canadian titanomagnetites could be reduced to 5 per cent, and by blending such a concentrate with titanium-free ores a mixture was obtained which could be smelted economically.[23] Titaniferous ores required much more fuel per ton of iron produced than did regular iron ores such as hematite.

Lyuban and Basov [24] concluded that the successful smelting of titaniferous magnetites depended upon the proper ratio of silicon dioxide to titanium dioxide in the charge, and to insure the proper proportions, silica was added as a flux. Experiments with Jehol iron ores, which contained 13 to 14 per cent titanium dioxide and 0.56 per cent vanadium pentoxide, revealed that by applying the principle of thermal dressing, the iron, together with the vanadium, could be recovered in the metallic state. [25] Titanium dioxide and other constituents went into the slag. Vanadium cast iron was produced in a blast furnace, with a slag containing 5 to 7 per cent titanium dioxide. [26] The losses of vanadium were smaller with a basic than with an acid slag. Fluidity of slags was sufficient in spite of the high titanium dioxide content. Zverev [27] observed that titanium dioxide did not give rise to abnormally high viscosity of slag, and, on the contrary, partial replacement of silica by titanic oxide resulted in a lowering. This thinning effect was more marked the more acid the original slag, and the first 2 to 4 per cent had the greatest effect. [28] Titanium dioxide lowered the surface tension of the slag. Slags containing up to 20 per cent titanium dioxide thickened very slowly in experimental graphite crucibles and in the blast furnace in an atmosphere of carbon dioxide and nitrogen, while those containing 30 per cent thickened considerably. [29] Such slags showed sharp transition from liquid to solid state, and thickening and solidification were attributed to the presence of finely divided carbide. From X-ray studies the principal component of basic slags was found to be perovskite, $CaO \cdot TiO_2$. [30] Titanium was reported to occur in intermediate to slightly basic blast-furnace slags formed at average temperatures as deoxidized rutile, and practically none of the element went into the iron. [31] Working with ultrabasic slags at higher temperatures and stronger reducing conditions, as in the electric furnace, the titanium occurred as dendritic crystals of the monoxide, fulvite. Korber [32] found less than 0.02 per cent titanium in the iron, even with a slag containing as high as 27 per cent of the dioxide, thus demonstrating the superiority of the element as a deoxidizer.

A sintered product containing 11.1 per cent titanium dioxide and 54.6 per cent iron was successfully smelted in an experimental blast furnace. [33] Slags containing more than 10 per cent titania offered difficulties. Sodium carbonate [34] and a mixture of calcium oxide and alumina [35] have been recommended as fluxing agents for titaniferous ores. Pavlov and Semik [36] periodically oxidized the slag, either by blowing air through it or by adding active oxidizers, such as pyro-

lusite, through the tuyères. This treatment transformed the lower oxides of titanium into higher, and consequently increased the fluidity of the slag. Balla [37] produced pig iron containing vanadium directly from titanomagnetite ores by adding to the charge small proportions of by-product vanadium aggregated turnings and open-hearth and Bessemer slags. To increase the entry of vanadium into the metal, the silica and alumina in the slag were maintained at 47 per cent. Loss of vanadium increased with increased proportions and acidity of the slag.

In a duplex process developed by Naito and Matsukato,[38] titaniferous iron ores were heated with an excess of lime or a mixture of lime and silica to form silicates, and the product was smelted with an excess of coke in a blast or reverberatory furnace to produce iron free from titanium. By working out the fusion of the slag, which contains lime, silica, and titanium dioxide, it is possible to calculate the various materials to be added to ores of any titanium content to get a fusible slag and obtain the iron.[39] Acid slags were produced. Ores containing titanium and much iron are smelted in the presence of coke with 9 to 32 parts of CaO and 12 to 37 parts of $Al_2O_3 \cdot MgO$ for each 100 parts of TiO_2 at 1650° C. Titanium collects in a fluid slag containing up to 65 per cent of the dioxide.[40] Magnesite and alkalies were added to the electric-furnace charge to produce a vanadium cast iron and a slag containing more than 70 per cent titanium dioxide.[41]

The direct smelting of titaniferous iron ores in the electric furnace, whereby the titanium was made to enter either the metal or the slag by controlling the temperature, was successfully accomplished, but they did not seem to offer any advantage over titanium-free ores under similar treatment.[42] High-quality gray cast iron was made by adding titanium to the molten metal and subjecting the mixture to the action of an oxidizing gas or a solid-oxidizing agent.[43]

Conditions for the formation of oxides and carbides of titanium, in connection with difficulties of furnace operation on titaniferous ores, were investigated by Soviet workers.[44] Reduction of titanium dioxide by solid carbon began at 927° C., and the carbide was formed at 900° to 1000° C. Hydrogen began to reduce the dioxide at 900° C., and its maximum effect, 26.3 per cent, took place at 1300° C. Carbon monoxide was a less energetic agent, and at 1300° C. only 7.9 per cent reduction took place; a mixture of the dioxide and sesquioxide was formed. Pure titanium carbide was obtained from a mixture of titanium dioxide and carbon after heating for 2 hours at 1850° to 1900° C.

Slags

From exhaustive studies of the melting point and viscosity, Cox and Lenox [45] concluded that no difficulty should be encountered in handling slags containing moderate amounts of titanic acid in the ordinary blast furnace. Melting points of slags containing from 1 to 14 per cent titania varied from 1270° to 1350° C., which was well within the workable range. The fluidity increased as the silica component was replaced by titanium dioxide. Titanium dioxide decreased the viscosity of acid slags at least up to a proportion of 17.3 per cent, and increased the viscosity of basic slags. [46] The monoxide, sesquioxide, and carbide increased the viscosity of both types. In the blast-furnace smelting of high titanium ores with slags low in ferrous oxide and manganous oxide, titanium passed into the slag in the form of the sesquioxide and monoxide, and decreased its fluidity. The carbide formed at higher temperatures. The melting-point diagram showed that titanium dioxide reduced the fusing point of calcium oxide and gave a more fluid melt. [47] It also lowered the fusing point of basic open-hearth furnace slag. [48]

At 1450° C., and in a reducing atmosphere, titanium dioxide in acid blast furnace slags exerted a strong desulfurizing action, [49] the degree of which increased to a maximum of 35 per cent as the titanium dioxide content increased to 10 per cent.

Viscous slags obtained from the reduction of titaniferous ores often retained drops of iron. This constituent was recovered by magnetic separation [50] after the slag had been disintegrated by the action of a jet of steam under pressure. Kakiuchi [51] was not able to effect a gravity separation of slags containing 8 to 20 per cent titanium dioxide from the pig iron produced. Titania added to various mixtures of calcium oxide, magnesium oxide, alumina, and silica in a graphite crucible at 1550° C. was in part reduced to lower oxides which gave the slag a bluish-black color.

Vanadium [52] has been obtained as a by-product from basic Martin slag produced in the smelting of Ural titanomagnetites.

Pig Iron

As early as 1863 it was recognized that pig iron produced from titaniferous iron ores had very great strength and excellent properties both for casting and for conversion. [53] The titanium appeared to impart a steely nature to the iron reduced from such ores, somewhat similar to that obtained by the use of manganese. That this benefi-

cial effect was due to the titanium was doubted by some workers, since none of the element could be detected in the iron by chemical analysis. Its value, however, was slowly accepted.

Titanium favors the precipitation of graphite in normally white cast iron and lowers the temperature at which the iron carbide decomposes.[54] It raises the point of transformation of pearlite and thus increases the speed of critical quenching of martensite, and lowers the thermal hysteresis of transformation. The element has the effect of lowering the temperature of graphitization of malleable iron, but does not affect the mechanical properties. In gray iron it produces a fine graphite of an eutectic appearance which limits itself at the grain boundary. Ferrotitanium does not diffuse satisfactorily throughout the molten metal, and a tertiary alloy containing silicon is considered the most effective means of introducing the metal. In general, titanium modifies the characteristics of cast iron in the same manner as silicon does. It favors the formation of ferrite in gray iron without any appreciable change in physical properties, and imparts to graphite a nodular form in which the grains are dispersed like those of an eutectic. In the presence of titanium, carbon dioxide bubbling through molten iron greatly refines the graphite, but if the metal is subjected to a reducing gas, such as hydrogen, the iron reverts to coarser graphite structure.[55] Below 4 per cent, titanium forms solid solutions with iron-carbon, and with larger proportions the solubility of carbon in the iron-titanium eutectic decreases.[56] It accelerates the graphitization of carbide.

According to Comstock,[57] commercial cast iron treated with ferrocarbontitanium frequently failed to show any increase in strength, probably because the alloy became soluble with difficulty and did not readily enter the molten mass. Preliminary tests showed, however, that iron, to which had been added 2 per cent of an alloy containing 15 to 20 per cent each of titanium and silicon, aluminum less than 1 per cent, and carbon less than 0.5 per cent, was 23 per cent stronger than the untreated standard. Another sample with 1 per cent of the alloy was 13 per cent stronger. The graphite particles in the titanium-treated products were fine, and there was a higher proportion of ferrite. Samples of cast iron, alloyed with 0.05 and 0.20 per cent titanium, in every case showed increased resistance to wear, and the tensile and bending strength increased with the percentage of the element present.[58] In a series of experiments, Feise[59] added powdered titanium metal to molten cast iron in the ladle in amounts of 0.25, 0.50, and 1.00 per cent, and found that the increase in tensile strength reached a maximum of 33 per cent at 0.25 per cent

addition, but fell off considerably as the additions were increased beyond this value. Three grades of gray cast iron containing various amounts of chromium, treated just before pouring with ferrotitanium, showed greater strength and hardness which increased with the amount of the alloy added.[60] The improvements were attributed to finer grained graphite and were more pronounced in the samples containing higher carbon or higher sulfur. Slocum[61] found that the addition of only 0.05 per cent titanium as ferroalloy increased the strength of cast iron 20 per cent.

In addition to increasing the tensile strength of cast iron, it rendered the metal more machinable, exerted a graphitizing influence, and acted as a deoxidizer.[62] The element was found to be especially effective in retarding crystal growth.[63] For example, an iron sample containing 0.12 per cent titanium showed a much finer structure than a similar material with only 0.09 per cent. In temper experiments at 1000° C. for periods up to 50 hours, it promoted a more rapid formation of a finer-grained temper carbon and a more rapid diminution of the total carbon content. Titanium carbide was very stable and remained unaltered in every test.

The addition of titanium to cast iron to promote the formation of fine-grained graphite increased the bending qualities 50 per cent or more. With increased titanium content, the resistance of the cast iron to acids and to corrosion in general was greatly increased.[64] The element showed a strong tendency to reduce the amount of common hardening constituents,[65] and raised the depth of chill in chilled castings.[66] According to Lobanov,[67] an increase in the titanium content of pig iron refined by the cupola-electric-furnace process affected the mechanical properties unfavorably. In alloying ferrotitanium with cast iron, cubically crystalline, whitish-gray carbide formed in the structure, and these inclusions were extremely hard.[68]

Two series of titanium cast irons were made by adding an aluminothermic alloy containing titanium 23.05, carbon 0.07, silicon 3.8, manganese 4.5, and aluminum 0.17 per cent, and traces of sulfur and phosphorus; and an electric-furnace product containing titanium 41.2, carbon 11.3, silicon 2.8, manganese 0.2, aluminum 0.6, phosphorus 0.01, and sulfur 0.02 per cent. The depth of hardening decreased with increased titanium content; all the samples were entirely pearlitic; 0.07 per cent titanium was sufficient to eliminate the free cementite; corrosion resistance was decreased somewhat with the increase in titanium. Physical properties decreased to a minimum with increase in titanium up to 0.09 per cent, and

then increased gradually. The temperature of the Curie point was independent of the titanium content.[69] The transformation curve showed that the gamma field was closed at 0.6 per cent titanium.[70]

The role of titanium in gray cast iron is essentially that of converting the carbon to graphite in very much the same manner as silicon, and of refining the flakes. This graphitizing effect of titanium may appear inconsistent, in view of its strong affinity for carbon in steel, but the difference is doubtless the result of the fact that the temperature is lower in cast iron. Titanium carbide formed at the high temperatures does not unite with iron or cementite, while the graphitizing action occurs at a lower temperature. This action is applied practically in many gray-iron foundries to close the grain or refine the structure of thick sections, with a resulting improvement in strength, and to prevent hard spots or chills in thin sections, which in turn improves the machinability of the casting.[71] The titanium as a ferroalloy is dissolved in the molten iron at ordinary temperatures, usually in the ladle just before pouring. A cast gray-iron compression cylinder has been exhibited in which the internal surface of the thick walls was dense and sound, and the thin outer ribs and flanges were not chilled, cracked, or misrun.

Castings from irons that solidify with a pearlitic cellular structure are more dense and less subject to shrinkage, and the addition of titanium assists materially in producing this type of structure.[72]

It is interesting to note that titanium was found in samples of nine ancient cast irons from China, more than 1000 years old.[73]

Purifying Steel

Before 1862 about a dozen patents were issued to Mushet, the pioneer British steelmaker, for the use and application of titanium in the manufacture of steel. Very beneficial results were claimed, and the value of the treatment was slowly accepted. Riley [74] examined many of these samples, and since he was not able in any case to detect more than a minute trace of titanium, he concluded that the element did not alloy with iron. He recognized the beneficial effect of such treatment, however, and attributed it to the action of titanium as a carrier of cyanogen to the steel as a result of its well-known affinity for carbon and nitrogen. Occasional reference to titanium as an alloying agent appeared in Europe early in this century, but until furnaces capable of operating at higher temperatures became available, much difficulty was encountered in getting

enough of the element into the solid steel to exhibit its beneficial effects.

Titanium metal of 75 per cent purity has been available commercially for many years, and since about 1931 a product containing 96 to 98 per cent of the element has been on the market. The price of around $5 a pound, however, restricts its use to minor proportions. In addition to high cost, much difficulty is encountered in dissolving the metal directly in molten iron or steel because of its high melting point, low specific gravity, and poor alloying qualities. Results obtained from such attempts have in general been unsatisfactory, so that titanium is used in metallurgy chiefly as a 15 to 25 per cent alloy with iron, which may also contain small proportions of carbon, aluminum, silicon, and other impurities, depending upon the method of manufacture. The melting point of such alloys increases and the specific gravity decreases with increasing titanium content, and even though products within this workable range of concentration have higher melting points than iron and steel, they dissolve readily in the fused metal. Other alloys, composed principally of iron and titanium together with small proportions of other elements such as boron, chromium, zirconium, and columbium, have been added to steel to develop special properties.[75]

Inasmuch as the available alloys are relatively expensive, titanium tetrachloride has been employed successfully as an agent for introducing titanium into baths of molten metal,[76] either alone or in conjunction with alloys. Furnace or ladle additions of titanium and silicon may be made to molten iron or steel in the form of exothermic silicides such as Ti_2Si, $TiSi_2$, and Ti_3Si_2.[77] The artificially prepared hydride,[78] titanium carbide[79] produced in the electric furnace, and the mineral, perovskite[80] (calcium titanate), may also be employed for this purpose.

Until about 1931, titanium was valued by most steel metallurgists as a scavenger or deoxidizer, rather than to produce new properties by its direct or alloying influence. In the former role, only 4 pounds per ton (except for high-carbon steel, notably for rails, which took up to 13 pounds per ton) were added to the ladle, and practically none of the element remained in the solid metal. The dioxide was more stable than oxides of iron, and, being a fluxing agent as well, tended to remove other oxides present in the steel.[81] It is well known that molten metals absorb considerable amounts of gases which are largely liberated as solidification takes place. For instance, oxygen and nitrogen dissolved from the air partly combine with the iron, but a large proportion separates out on cooling to form blowholes

or other imperfections in the ingots or castings. The desirable physical properties of many special steels are determined primarily by the reduction of oxides and the removal of occluded oxygen by a metal having a higher affinity for the gas, but there are few elements that combine with nitrogen and remove its influence from the metal. Titanium unites with both gases to form stable compounds, and the earlier literature is replete with statements as to its value as a nitrogen remover.[82] It was naturally inferred that additions of the metal would have the same effect on nitrogen as on oxygen, but the difference lies in the properties of the products formed. For example, the dioxide formed by reaction of titanium with oxygen is insoluble in steel and is readily removed as a slag, while the nitride, being highly metallic, is soluble and consequently not so easily separated. It has even been proposed that titanium be employed for causing nitrogen absorption in nitriding steel. The element transforms the nitrogen from combination with iron to a less harmful form, somewhat as manganese does sulfur.

The metal is very effective in removing gas bubbles from steel, since it takes up nitrogen as well as oxygen to form high-melting compounds. Improvement in mechanical properties is due primarily to this removal of gases, rather than to the formation of a titanium-iron alloy.[83] For removing the last traces of oxygen and nitrogen, the titanium should be added to the ladle in the form of a ferroalloy, and time should be allowed for the slag to rise.[84] It further prevents segregation and blowholes, aids the removal of sulfur and phosphorus, and increases the strength, endurance, and wearing property of the steel.

Comstock[85] found titanium to be more effective than aluminum as a scavenger and deoxidizer of steel. Critchett and Crafts[86] recommended an alloy containing titanium, along with silicon and aluminum, vanadium and calcium, for deoxidizing ferrous metals in general. Silicotitanium[87] has been employed as a graphitizing agent in high-resistance irons.

Alloys reported to be more effective than ferrotitanium for deoxidizing iron and steel contained boron 0.25 to 5.0 per cent, titanium 5 to 25 per cent, aluminum 5 to 25 per cent, manganese 5 to 30 per cent, silicon 10 to 40 per cent, and the remainder iron;[88] aluminum 45 to 60 per cent, silicon 20 to 30 per cent, titanium 8 to 15 per cent, and iron.[89]

In an experimental study, titanium-treated steels were much less segregated and were accompanied by fewer pipes.[90] In small amounts it eliminated oxygen reducible by carbon, and in larger

proportions decreased the nitrogen combined with iron and manganese. A portion, at least, of the nitrogen remained in the steel, combined as minute violet or orange inclusions. Microscopic, X-ray, and analytical studies of quenched steels suggested a series of solid solutions of titanium carbide and nitride.[91] According to Cornelius and Bollenrath,[92] steels with appreciable carbon content hardly absorb titanium at all. A carbon film formed on the surface of the molten metal, blocked the penetration of the stable carbide-forming elements, and impeded the diffusion of elements which limited the γ region but did not form carbides.

Nitrogen has been incorporated into steels by adding titanium cyanonitride in the charge.[93] Steels may be hardened by nitrification, and this may be effected by adding titanium in excess of the amount required for the fixation of the nitrogen, but less than 0.25 per cent.[94] Similarly, the drawability may be improved by controlling the nitrogen in this manner.[95]

The effectiveness of titanium in effervescing sheet bars for manufacture into galvanized sheets and tin plate is universally accepted. Addition, as an alloy with iron, improves the surface of steel sheet and reduces pinholes in the coating. Automobile body stock, high-grade structural steels, and deep stampings may be similarly treated to advantage, as well as certain alloy steels. Ferrotitanium has been used in the treatment of steel and iron rolls where high resistance to shock and abrasion is important; stocks for castings in foundry practice, low- or high-carbon steels for making chains, gears, pinions, ties, die plates and heads, propeller shafts, driving rods, and other forgings; for tool (crucible) steel; cast-iron ingot molds; steel for acid pots and for chilled car wheels; and for many machine parts.

The first really important use of titanium in metallurgy was to purify Bessemer rail steel, and 256,759 tons were so treated in 1910. With the development of the open-hearth process, however, consumption in this field dropped rapidly, until at the present time an insignificant tonnage is treated in this manner. Although the addition of titanium also improves open-hearth rails, this is not necessary to produce a product within the required specifications. In the meantime, ferroalloys of titanium found other applications in the iron and steel industry and in nonferrous alloys, and production seems to have more than held its own.

The principal function was as a flux, and this cleansing effect increased the solidity and purity of the metal. These properties had marked influence on the mechanical structure, prevented break-

down under heavy rolling load, and reduced wear resulting from abrasion. Sulfur and phosphorus were not reduced by the treatment. In the manufacture of Bessemer steel, 1 per cent of the crushed ferroalloy, containing 10 to 15 per cent titanium and 5 to 7 per cent carbon, was added to the ladle as the steel was poured from the converter.[96] A study by Fitzgerald [97] revealed that of 78 Bessemer heats without titanium treatment, only 36 per cent gave A-grade rails within specification limits, while 78 per cent of the rails from steels to which titanium had been added to the ladle passed inspection. Comparative tests, conducted by the New York Central Railroad on a sharp curve bearing heavy traffic, showed that in 6 months' service the flange wear of titanium-purified rails was 1.1 pounds per yard as against 3.6 pounds for the regular Bessemer rails.[98] According to Janssen,[99] life of rails and gears from titanium-treated stock was about 50 per cent longer than similar products made of ordinary steel and subjected to the same service. Quick [100] made a comparison of rails made from titanium-treated and silicon-treated open-hearth steel in actual service from 1922 to 1927. No transverse fissure was noted in the rails from 20 heats of the titanium-treated stock, while eight such defects were reported in the comparison rails from 23 heats of silicon-treated steel. In another test extending from 1920 to 1937, seven transverse fissures were reported in the rails from 20 heats of titanium-treated steel, and 177 in comparison rails from 92 heats of steel with no addition of this element. During 16 years in heavy traffic, 52.5 per cent of the titanium-treated and 64.5 per cent of the silicon-treated rails were replaced for various reasons.

The successful use of titanium in treating iron and steel has been well established, but under normal conditions it appears that titanium is too expensive for use as a general deoxidizer and that it can be employed economically only for a final scavenging after ferromanganese or ferrosilicon has done most of the work. Even for killing steel in the ingot molds, aluminum appears to be less expensive.

For special purification and for alloying purposes, however, costs are frequently less important than better performance of the finished steel, but it always has to be considered. With the exception of aluminum and vanadium, titanium has a greater avidity for oxygen than any other metallic element commercially available for steelmaking, and this great chemical activity, which is the basis of the effectiveness of the element in steelmaking, is one of the reasons the alloys are difficult and expensive to make.

Alloying Agent in Iron and Steel

Northcott and McLean [101] studied the effect of additions of up to 6.0 per cent titanium to plain carbon and alloy steels. A quenching temperature of 1235° C. is required to insure solution of the titanium carbide. Titanium increases the hardenability to about the same extent as chromium. The effect of the metal is the resultant of three separate effects: the strong affinity between titanium and carbon, displacement of the gamma region to higher carbon contents, and the precipitation hardening type of solid solubility curve for titanium in ferrite. Additions of titanium to steel have been reported to increase the transversal strength 17 to 23 per cent. [102] Small traces of the element produced a very fine grain in carbon steels and also in alloys of the ferrochromium type which did not pass through a transformation in the solid state. Since heat treatment did not affect the structure of such materials, the properties were improved by developing a fine grain-size in this manner. [103] The period of austenite grain growth, which started after the incubation period, tended to produce nonuniformity of grain size. Addition of 0.1 per cent titanium, however, maintained fine grain up to 1050° C. in the cast condition, but after forging the stability of the fine-grain condition did not differ from ordinary steel. [104] Additions up to a certain maximum value improved the quenching effect, but proportions beyond this range resulted in an impairment. [105] The element entirely suppressed the undercooling [106] of steel, and in small amounts notably influenced the amount of decarbonization of iron-carbon alloys containing up to 1.7 per cent of the latter constituent. [107]

According to Bolsover, [108] red shortness in steel, due to liquid sulfide at elevated temperature, was eliminated by the use of titanium. Correctly applied, it retarded segregation of sulfur, phosphorus, and carbon in normally quick-setting steel, [109] and raised the temperature of transformation points. [110] This effect was more pronounced in low-carbon 13 per cent chromium steel; for example 0.11, 0.14, and 0.60 per cent of titanium raised the transformation point to 800°, 900°, and above 1140° C., respectively.

Gaev [111] found that the element began to diffuse into the lattice at 1300° C., and that it formed an eutectic melting at 1340° C. The carbides did not dissolve in the iron solid solutions at temperatures up to 1300° C., and the nitrides did not dissolve in molten steel at 1500° C. Titanium had a softening effect on low-carbon manganese steel (1.56 to 1.83 per cent), and its beneficial influence on the duc-

tility and impact strength was greater than that of vanadium. Residual titanium of 0.1 per cent or more in forging steels prevented formation of coarse dendrites and raised the coarsening temperature to above 1950° F.[112] A ferroalloy containing 25 per cent vanadium, 15 per cent titanium, and 10 per cent aluminum, added in very small amounts in the final stages of steelmaking, yielded products of excellent uniformity and imparted high toughness as well as high hardness in coarse-grained and fine-grained products.[113]

According to Wasmuht,[114] precipitation hardness of iron was effected at a titanium content of over 3 per cent, and in the presence of nickel or silicon this hardening action was promoted. That is, less titanium was required. Carbon had the opposite effect. Additions of up to 0.4 per cent to plain carbon structural steel (0.1 to 0.25 per cent carbon) seemed to improve the yield point and tensile strength considerably without seriously affecting the elongation or reduction of area.[115] High tensile strength and elastic limit, along with a fairly high elongation, were obtained in a steel containing 1.32 per cent silicon and 0.42 per cent titanium.[116] Additions of titanium increased the yield point and tensile strength, and amounts up to 0.17 per cent increased the coarsening temperature.[117] According to Belorusov, Pakhar, and Fridrikhsen,[118] raising the titanium content from 0.01 to 0.04 per cent showed no further increase in tensile strength, but increased the elastic limit. After cooling in the furnace from 930° C., the elastic limit disappeared, with the complete binding of the carbon as carbide.[119] Better mechanical properties were developed by quenching in water, followed by tempering with a 1 per cent titanium steel, than with an ordinary steel without this constituent. It increased hardness and imparted exceedingly high tensile strength, while a small elongation was retained. In low-carbon steels it showed a definite tendency to form carbides and diminished the extent of strain-age hardening.[120] In steels containing 0.20 to 0.25 per cent carbon, titanium in amounts of 1.97 per cent or less eliminated hardenability.[121] It combined with all the carbon present to form the carbide, which was soluble in the metal at 2500° F. and therefore subject to rearrangement by heat. The steel was not hardened by solution of the compound. Roedeker[122] found that steel containing 0.9 per cent of this metal inclined to red brittleness, while with 1.3 per cent it did not. Addition of titanium decreased the crack sensitivity because of the formation of extremely stable carbides[123] and imparted deep hardenability combined with great toughness.[124] In 1 per cent chromium steel it raised coarsening

temperature, lowered the strength, and increased ductility and impact values.[125] Small proportions contributed markedly to tensile strength and yield point.[126] In general, titanium up to 0.1 per cent increased the hardenability effectively, while above 0.2 per cent the effect decreased proportionately, and with sufficient titanium it was lost entirely.[127] The hardenability factors for titanium can be based on acid-soluble instead of total titanium, provided that account is taken of the fact that the insoluble portion decreases hardenability by rendering ineffective a proportionate amount of carbon. In small proportions, titanium exerts a stronger influence on hardenability than has been found for any other element except boron. The sensitivity of high-speed molybdenum steels to overheating can be reduced by the addition of 0.15 per cent titanium.[128] Final addition of titanium to an acid electric heat assisted in deoxidation, but was most useful in increasing hardenability and in producing a fine-grained product.[129] Stevens[130] employed an alloy containing 6 to 50 per cent titanium, 6 to 50 per cent vanadium, columbium, tantalum, or uranium, less than 20 per cent silicon, and the remainder iron to impart toughness and hardenability to plain carbon steel or low-alloy steels.

Ferrocarbontitanium has been employed with considerable success to replace part of the aluminum normally added to produce fine-grained steels and to improve cleanliness and uniformity of the product.[131] During World War I, one manufacturer reduced the ferromanganese requirement 50 per cent by adding sufficient ferrotitanium to the ladle. In the production of intermediate manganese steel, ferrocarbon titanium may replace more expensive alloys, notably nickel and vanadium.[132]

The resistance of tin plate to perforations was increased by addition of titanium to the ladle in the manufacturing process.[133] It has also been added to the molten bath to deoxide and degasify low metalloid steel for use as vitreous enamel stock.[134] In small proportions it showed improvement in pearlitic manganese steel.[135] An armor-plate steel contained 0.1 to 0.4 per cent titanium, 0.1 to 1.5 per cent carbon, and 1.0 to 4.0 per cent silicon.[136]

Titanium improved the forging properties and prevented trans-crystallization in heat-resisting steel containing 10 per cent aluminum.[137] Structural steel containing 0.1 to 0.2 per cent of this element possessed a minimum ultimate strength of 85,000 p.s.i. with good toughness.[138] Seven-tenths per cent imparted scale resistance to medium chromium heat-resistant steel, but lowered the mechanical properties.[139] The effect of titanium and other elements on the

corrosion resistance of iron and steel under many conditions was summarized by Tice.[140]

High-temperature strength of steel was increased by introducing a carbide-forming element such as titanium.[141] Addition of relatively small amounts decreased hardness, and higher proportions had the effect of throwing the steel beyond the alpha loop, thus eliminating the critical range. Addition of titanium, in the form of a ferroalloy containing more than 20 per cent of the element, was reported likely to give rise to segregation.[142] Hardness increased with the titanium content. Such a steel was prepared directly by heating refined iron at 1700° to 1750° C. in an electric furnace, with the necessary amount of titanium.[143]

The iron-titanium constitution diagram [144] indicates that titanium, as an alloying element in steel, can be used for strengthening and hardening the austenitic highly alloyed steels that are not hardenable by heat treatment in the usual manner. Alloys containing 25 per cent titanium have $\frac{1}{10}$ the corrosion rate of iron.

Carbon Control; Stainless Steel

For carbon control,[145] titanium is used as an alloying element in steel. As a result of the strong affinity of this element for carbon, and of the relatively low solubility of the resulting carbide in the solid metal, additions of appropriate amounts to steels virtually serve to remove all carbon from participation in the physical changes which normally take place on cooling, so that for all practical purposes the product has the characteristics of steel with almost no carbon. It is difficult and expensive to produce very low carbon steel, 0.02 per cent or lower, but the same results may be obtained more conveniently by adding titanium. In a study of iron-titanium-carbon steels, practically all the titanium was found to be present as the carbide if the weight ratio of titanium to carbon in the alloy was less than 4.[146] A double or complex carbide was not formed.

Carbon is undesirable in some steels, particularly the chrome, nickel, stainless types, and it is often more economical to neutralize rather than remove small amounts. To accomplish this end, titanium in proportions of 5 to 7 times the carbon content is added to the molten metal. Steel treated in this manner has improved resistance to corrosion and is soft and machinable. This improved workability results from elimination of age-hardening effects, but titanium itself may encourage age hardening if a considerable excess over that required for carbon control is present.[147]

In proper proportions it effectively locks up the carbon in certain types of alloy steels so as to prevent its combining with other elements, thus robbing the matrix of one or more essential constituent.[148] For instance, in stainless steels it inhibits intergranular corrosion. Instead of the hardening effect normally imparted by the chromium and carbon, steels so treated with titanium are characterized by the facility with which they may be hot-worked, by their relative freedom from air hardening, and by their ductility and softness in the as-rolled condition.

A peculiar form of deterioration often occurred on heating austenite stainless steel to 900° to 1500° F., as in welding, which caused embrittlement and loss of corrosion resistance at the grain boundaries. This failure was attributed to precipitation of chromium carbide, which removed chromium from the austenite solid solution and thus lowered the resistance to corrosion. Titanium added to the alloy was found to take care of the carbon effectively, so that the austenite was not altered and the corrosion resistance of the steel was maintained even after heating.[149] With carbon held securely in combination with the titanium, it cannot rob the solid solution of chromium to form the carbide at the grain boundaries, and the corrosion resistance of the product is maintained at all points. The addition of an excessive proportion of titanium to 18-8 stainless steels results in an undesirable age-hardening effect and should be avoided.

Steels with more than 4 per cent chromium and 0.02 per cent carbon are decidedly air-hardening, because of the action of the chromium in slowing the rate of transformation, with the result that sorbite or martensite is retained in the mass at normal rates of cooling in air. Titanium added to the molten metal forms the less-soluble titanium carbide, leaving the ground mass practically free from carbon so that martensite cannot form to exert this harmful effect. This treatment yields relatively soft steels of ferritic structure with fine cyanonitride crystals. It is much stronger than mild steel, in contrast to similar products without titanium.

Although titanium should be present in high chromium steels in a ratio of 5 to 7 times the carbon, smaller proportions afford some improvement. Large excesses are detrimental through hardening of the solid solution of iron and chromium. Wyche[150] recommended that a 5 to 1 minimum ratio of titanium to carbon should be employed in 18-8 stainless steel because part of the titanium is rendered inactive by combining with nitrogen and oxygen. In air welding both 18-8 titanium and 18-8 columbium stainless steel, it was necessary to employ columbium-bearing rods. These steels may be hot-

worked readily. The addition of 0.90 per cent titanium to a stock containing 5.93 per cent chromium raised the Ac_1 point from 803° to 898° C., and on cooling raised the Ac_1 point from 436° to 841° C.[151] The austenite structure of an 18-8 stainless steel was altered by titanium in steps from pure ferrite to pure austenite, depending upon the percentage added. Such a treatment decreased the toughness appreciably, while the resistance to corrosion decreased with increase in the titanium content and with increase in hardness.[152] Iron alloys containing 25 per cent or more chromium solidified with coarse grains and were brittle. The ferrite in such materials had no transformation point, so that grain refining by heat treatment was impossible. Nitrogen produced a fine-grained product, and titanium cyanonitride was an excellent source of the element.[153] In low-carbon stainless chromium steels, 0.5 per cent titanium entirely suppressed the dendritic zone in ingots and increased grain growth. It rendered the steel ferritic and decreased the heat resistance.[154] The element reduced air hardening in low-chromium steels (2 to 6 per cent), but such products did not retain their toughness as well as those containing columbium.[155] High-carbon stainless steels containing, for example, 16.81 per cent chromium, 7.86 per cent nickel, 0.46 per cent carbon, and 0.11 per cent titanium showed a maximum hardness of 33 Rockwell C after quenching from 1000° C.[156] The value was higher than for similar steels without titanium. Thermal, X-ray, and structure examinations of the system iron-chromium-titanium, up to 57 per cent of the latter component, showed primary segregations from the melt of tertiary solid solutions of alpha iron with chromium and titanium, tertiary solid solution of Fe_2Ti with alpha iron and chromium, and Cr_2Ti_3.[157] A ternary eutectic point was observed at 1420° C., and the ternary solid solutions contained less than 0.2 per cent titanium.

Small additions of titanium to 14 per cent stainless steel increased the resistance to corrosion by sea water and by boiling nitric acid solutions, and improved the mechanical properties.[158] Similar additions to permalloy more than doubled the initial magnetic permeability and decreased the coercive force one third. As little as 0.14 per cent titanium increased the yield strength of chrome-manganese stainless steels 15 to 20 per cent, while ductility and impact resistance were not impaired.[159] Titanium and columbium improved the resistance to scaling of 18-8 chrome-nickel steel.[160] Titanium-phosphorus steels are not subject to temper hardening or to temper brittleness, can be welded successfully, and are tough at low temperatures.[161]

Applications of Titanium Alloy Steels

A marked increase in the yield strength can be obtained by the appropriate aging of cold-rolled sheets of austenite stainless steel containing 0.5 per cent titanium. This stock was suitable for aircraft construction.[162] From 1 to 5 per cent of the element has been used in austenitic nickel steels for parts of gas turbines [163] that need high creep strength at 600° to 800° C., and in austenite, nickel-chromium-cobalt alloys suitable for constitutional material for use at high temperatures.[164] A stainless iron-chromium alloy containing up to 3 per cent of this element exhibited good working properties and resistance to wear for sand nozzles and pumps.[165] It has been used in proportions of 0.3 to 1.5 per cent in chrome-nickel steel for use at high temperatures, as in automobile valves,[166] and in austenitic nickel steel for the manufacture of compensating spiral springs for chronometers to modify the thermoelastic properties.[167] Steel containing 16 to 30 per cent chromium, not over 0.3 per cent carbon, and from 0.6 to 2.2 per cent titanium, has been recommended for making seamless tubes.[168]

Chemical reactions involving high temperatures and pressure in the presence of hydrogen and sulfur compounds were carried out in vessels made of or coated with a titanium alloy.[169] A typical composition contained 92 per cent iron, 4 per cent titanium, 3 per cent nickel, and 1 per cent chromium. The increased resistance of such steels was attributed to the substitution of very stable special carbides (TiC) for the usual form (Fe_3C).[170] A 2.5 per cent chromium-titanium steel showed good mechanical properties and creep resistance in equipment for ammonia synthesis.[171] Tanks of 18-8 stainless steel containing titanium were used for handling hydrogen peroxide.[172] Cast iron or steel containing up to 1 per cent each of titanium and copper was used for making articles required to resist corrosive action of sea water and moist air.[173] Hydrogenation apparatus made of titanium steel exhibited improved resistance to the gas.[174] Ordinary steels were effective up to 700° to 725° C. A special chrome-nickel stock containing 0.75 per cent titanium was extremely serviceable for urea synthesis apparatus.[175] Of a number of stainless steels investigated by Gurovich,[176] only those containing titanium were resistant to moist iodine vapor.

High cobalt and chromium steel alloys for springs capable of being hardened by heat contained 1 per cent titanium,[177] and from 0.2 to 5 per cent of this constituent was added to high cobalt steel

for making die casting molds and similar apparatus to be subjected to heat.[178] An alloy steel containing carbon up to 0.25, silicon 0.1 to 1.5, manganese 0.2 to 5, copper 0.05 to 4.5, chromium 5 to 18, titanium up to 10 per cent exhibited good resistance to high temperature and pressure.[179]

Addition of titanium to chrome-molybdenum steel improved its creep strength in the hot-rolled and tempered condition,[180] and such a product for airplane tubing showed improved bending qualities and better ductility, impact value, and microstructure.[181] Tubes for oil heaters made of steel containing 5 per cent chromium, 0.5 per cent molybdenum, 1 per cent silicon, and 0.39 per cent titanium showed good oxidation resistance up to 1600° F.[182] Corrosion-resistant steel of this type, capable of being cold-worked, had 0.5 to 3.5 per cent titanium.[183]

Titanium has been used in place of the more expensive vanadium in steels for high-speed tools.[184] Such a product contained 18 per cent tungsten, 4 per cent chromium, and 1 to 1.5 per cent titanium. A similar composition contained 2.1 to 15 per cent titanium, 0.7 to 1.8 per cent carbon, and 0.3 per cent vanadium.[185] Such an alloy containing cobalt 10 to 40, tungsten or molybdenum 10 to 30, carbon not over 0.4, nickel 0.3 to 10, titanium 0.3 to 3, chromium 5, and vanadium up to 5 per cent was easily welded and was suitable for cutting tools.[186] Another, composed of 38 to 48 per cent cobalt, 28 to 38 per cent chromium, 16 per cent tungsten, 2.5 per cent carbon, 0.2 per cent boron, and 3 per cent titanium, was suitable for high-speed cutting tools.[187] Small proportions of this constituent, 0.12 to 0.38 per cent, improved the cutting properties of chromium-silicon-vanadium high-speed steel.[188] In proportions up to 1 per cent it has been employed in tungsten steel for making welded tubes capable of withstanding high pressures.[189] Serviceable turbine buckets have been made from titanium-bearing silico-tungsten-chromium steel.[190] Titanium is an important element in alloys for high-temperature service in gas turbines, jet propulsion parts, and turbosuperchargers.[191] High-temperature stainless steels for gas turbines contained 0.65 to 1.2 per cent titanium.[192] The pistons and cylinder heads of internal-combustion engines or parts of internal-combustion turbines can be made of an alloy containing a small proportion of titanium with chromium, nickel, magnesium, copper, silicon, and iron.[193] Alloys containing 0.05 to 0.60 per cent titanium, along with 2.25 to 4.0 per cent carbon, 1.5 to 3.5 per cent silicon, 0.6 to 1.25 per cent phosphorus, 0.3 to 1.0 per cent manganese, and 0.5 to 2.0 per cent chromium, showed good wear resistance and were

suitable for cylinder liners, pistons, piston rings, and valves of internal-combustion engines.[194]

An iron-chromium alloy for coating, bonding, or edging steel articles contained 0.3 to 1.5 per cent titanium.[195] Most defects in vitreous enameling of iron result from the reaction of an iron-carbon aggregate with molten glass. Such aggregates may be eliminated on a commercial scale by treating low-carbon iron, produced in an open-hearth furnace, with sufficient titanium to combine with all the carbon, a ratio of 5 to 1.[196] This stabilized enameling iron made practical the one-coat vitreous enamel finish.

By using very pure materials, iron and iron alloys may be obtained with magnetic permeability up to 50,000, as compared with 6000 to 8000 in the best grades of commercial materials, and with a hysteresis loss as low as 600 ergs per cubic centimeter per cycle.[197] The addition of titanium in small amounts was found to give higher magnetization curves and lower hysteresis losses, which were attributed to the cleansing action of this element.[198] However, if enough was added that some remained in the solid metal the magnetic properties were lower than in the untreated material. Similar results were obtained by Applegate,[199] who found that addition of up to 1 per cent pure titanium to Swedish charcoal iron lowered the hysteresis losses and increased the permeability, but that higher proportions produced the opposite effect. The common ferroalloys did not improve the magnetic properties of iron to the same degree as the pure metal. Ferrotitanium alloys could not be softened by long annealing at 760° C.

The magnetic and technologic properties of silicon steel were improved by introducing up to 0.1 per cent titanium.[200] Iron alloys containing 2 to 5 per cent silicon and up to 0.8 per cent of this constituent had low energy-loss measurements in transformers.[201] Additions of 0.09 per cent to 4 per cent silicon steel stock for transformer cores greatly refined the dendritic zone and increased the grain size of the crystallization obtained by heat treatment.[202]

Castings

In making steel castings, titanium as an alloy with iron is added to the molten metal after the ferrosilicon and ferromanganese, and the product is held in the ladle for 5 to 10 minutes to permit the deoxidation reaction to proceed to completion. The mass does not chill, since heat is liberated by the reaction. As a deoxidizer, vanadium is only 70 per cent as effective as titanium and has little in-

fluence on the nitrogen.[203] According to Slocum,[204] the principal value of titanium in steel casting is for the removal of nitrogen and elimination of one of the factors which produce blowholes. In an extensive study Duma [205] employed titanium as a degasifying and cleansing agent in electric-furnace production of castings of medium- and low-carbon, copper-bearing, and stainless steels and monel metal in amounts of approximately 0.1 to 2.0 per cent. In proportions less than 0.4 per cent it improved the strength and hardness considerably without appreciable decrease in ductility and impact-resistance. Weldability, machinability, and resistance to corrosion were not decreased, and particularly with stainless steels these properties showed marked improvement.

Titanium prevented air hardening and lowered the yield and tensile strength of chromium steel castings.[206] Copper-bearing cast steels containing a small amount of this constituent showed high strength.[207] The forging properties and toughness of high-chromium corrosion-resistant cast iron were improved by this metal.[208] Additions of ferrosilicontitanium and ferrocarbontitanium increased the tendency of whiteheart malleable cast iron to graphitize.[209] The depth of chill in iron castings was decreased.[210] Addition of titanium containing pig iron to a charge for casting molds lowered the hardness of the metal, comminuted the graphite inclusions, and induced a more uniform structure.[211]

Bogachev and Nekhaeva [212] studied a number of cast irons containing 0.75 to 1.3 per cent titanium. The titanium appeared as cyanonitride having the composition 71 per cent titanium, 17 per cent carbon, and 3 per cent nitrogen. No titanium was present in solid solution. The carbonitride decomposed in an oxidizing atmosphere and was transformed partially into oxides and partially into solid solution. Titanium as cyanonitride had no effect upon the structure of the iron, did not affect A_1, and decreased the hardness along the cross section. In general, titanium did not improve mechanical properties and made casting properties worse. Proportions above 0.7 per cent were not considered desirable.

Nekrytyi [213] found that additions of titanium aided the recovery of scrap from war materials which contained various alloying agents and rust by comminuting precipitated graphite and generally inducing a fine-grained structure. Because of its great affinity for carbon, oxygen, and nitrogen, titanium appeared in pig iron as the cyanonitride, and if air was excluded the carbide formed. It proved more effective if added in powdered form to the ladle shortly before casting than if added to the furnace charge.

Chapter 22

NONFERROUS METALS AND ALLOYS

Nickel

One of the earliest important applications of titanium as an alloying element was in the Konel alloys which were developed in 1929. A typical composition consists of 73 per cent nickel, 17 per cent cobalt, 7.5 per cent iron, and 2.5 per cent titanium. These platinum-like alloys have remarkable tensile strength and stiffness at high temperatures as a result of the age-hardening properties conferred by the titanium. The hardening constituent has been reported to be Fe_3Ti.[1] According to Pilling and Talbot,[2] the age-hardening dispersive in Invar and Elinvar is Ni_2Ti, and its precipitation displaces the range of characteristic properties to appreciably higher nickel contents.

Nickel and its alloys having red shortness as a result of a preliminary deoxidizing and malleabilizing treatment were freed from this and other defects by adding to the mass, while molten, a controlled and critical amount of titanium and of boron or phosphorus.[3] The solidified product was free from seams, splits, cracks, and red shortness, and had a degree of malleability permitting working with standard mill equipment.

Proportions up to 1 per cent have been employed in nickel alloys for cathodes.[4] A product containing, in addition to the nickel, 0.25 per cent titanium, 1 per cent carbon, 0.25 per cent magnesium, 0.55 per cent silicon, 0.35 per cent cobalt, 0.14 per cent iron, 0.10 per cent copper, and 0.12 per cent manganese, could be rolled free from cracks. Titanium in small proportions increased the coercive force and decreased the reduction by a corresponding amount of an alloy containing 20 to 28 per cent nickel, 9 to 15 per cent aluminum, and the remainder iron.[5] Moldable chrome-nickel alloys, capable of annealing or tempering, contained from 0.5 to 5.0 per cent titanium.[6] An alloy containing nickel 40 to 50, cobalt 20 to 30, chromium 15 to 30, iron 5 to 15, and titanium 1 to 4 per cent showed tensile properties at 1110° C. approximately 80 per cent of those at room temperature.[7]

Alloys of similar composition were used for exhaust valves of automobiles and other parts exposed to high temperature.[8] The cavitation resistance of a nickel-titanium-beryllium alloy under water impact was reported to be exceptional.[9] Parker[10] produced an alloy, having high strength at machinable temperatures at 1200° to 1600° F., consisting of 3 per cent titanium, together with nickel 55, molybdenum 20, manganese 2, selenium 0.25 per cent, and the remainder iron. Titanium from 2 to 4 per cent has been employed in a nickel alloy having good oxidation resistance up to 1650° F.[11] A precipitation-hardened, super-heat-resistant alloy reported by Gordon[12] contained 2 per cent titanium with 42 per cent nickel, 22 per cent cobalt, 18 per cent chromium, and 14 per cent iron. Bieber and Buck[13] produced an age-hardenable nickel alloy containing 0.29 to 2.0 per cent titanium. Such alloys were hot-rolled to thin sections,[14] had a low coefficient of thermal expansion,[15] had a high hardness, and were suitable for age hardening.[16] A nickel alloy containing 1.0 to 2.5 per cent beryllium and 0.5 to 4.0 per cent titanium has been used for making parts requiring high alternating stress resistance, and particularly where torsion fatigue resistance is required.[17] In compositions of this type, nickel forms compounds with the titanium, such as Ni_3Ti.[18]

Nickel-chromium alloys containing titanium have high strength at temperatures up to 1500° F. and are suited for gas turbine service, as a spring material operating at high temperatures, and as manifold and tail pipes of airplanes.[19] The alloy has good casting qualities and is resistant to thermal shock. A high-density alloy contains titanium alloyed with heavier metals such as molybdenum, tantalum, platinum, and tungsten.[20]

Copper

A very marked age hardening occurs in copper alloys containing 0.8 to 4.8 per cent titanium which increases the stiffness and strength and slightly decreases the ductility of forged bars.[21] The age-hardening effect of titanium is similar to that of the more expensive beryllium.

Copper with 10 per cent titanium, manganese with 30 per cent, aluminum with 7 per cent (Webbite), and similar compositions have been employed to a limited extent as deoxidizers and degasifiers for copper and other nonferrous alloys.[22] Titanium in these alloys refines the grain size, increases strength, and promotes soundness. In cast copper and in copper-base alloys, high strength without undue loss of electrical conductivity may be obtained by incorporation of

up to 1 per cent titanium, followed by suitable heat treatment. A copper-base alloy containing 2 to 50 per cent nickel and 1 to 10 per cent titanium showed good strength and hardness.[23] Improved physiochemical properties of an alloy containing 1.3 to 2.6 per cent beryllium were developed by introducing up to 0.5 per cent titanium.[24]

Titanium has been employed in copper alloys for springs and needles as a stabilizing agent for the beryllium component.[25] The addition of up to 0.3 per cent to aluminum-copper alloys produced a fine grained structure which appreciably increased the strength.[26] Alexander[27] applied a thin layer of titanium hydride to copper surfaces and heated the system in an atmosphere of hydrogen above 875°C. to produce an alloy coating. The titanium and copper diffused into one another and flowed over the entire surface. Similarly, Bernstoff and Allendorfer[28] mixed titanium metal in finely divided condition with copper, nickel, molybdenum, or iron, enclosed the mixture in a casing of the latter metal, and heated below the melting point to form a preliminary alloy by diffusion of the metals into one another.

Alloys of titanium with copper, nickel, or silver were prepared by gradually heating a mixture of the powdered metal and titanium hydride in a vacuum furnace at 1000° C. At 350° C. the hydride began to decompose, the hydrogen removed all traces of nitrogen and oxygen contained in the charge, and the mass gradually became compacted.[29]

Aluminum

In aluminum and its alloys, titanium is added primarily to effect removal of the gases and to refine the grain.[30] The function is quite different from that in iron, steel, copper, and nickel, in that it neither deoxidizes the aluminum nor produces any hardening after aging, nor holds any undesirable impurity in harmless combination. The compound $TiAl_3$ is formed. It precipitates from the cooling melt at a relatively high temperature in the form of a great number of fine, isolated needles which serve as nuclei for the crystallization of the main body of the mass as the temperature is further decreased. With such a large number of centers of growth in a unit volume many crystals are started, where otherwise there would be only a few. The result is that none of them is able to grow so large. The fine grain size naturally improves the strength of the product, and increases of 10 to 25 per cent may be attained. In a specific test the tensile strength was increased from 17,000 to 22,000 p.s.i. As a

result of the small crystal size and the elimination of gases, resistance to leaking of castings produced from such alloys was much better than that of similar materials without the titanium. In actual tests, additions of only 0.15 to 0.20 per cent of this element to the common alloy, consisting of 92 per cent aluminum and 8 per cent copper, gave a much finer grain with the same pouring temperature and size of casting.

The titanium may be added in the form of a 7 per cent alloy in aluminum or as anhydrous titanic chloride, but in general the alloy is more effective. Incorporation of more than 0.4 per cent has not been found necessary or advisable. Additions of titanium tetrachloride decreased the grain size of aluminum alloys, increased the density, and improved mechanical properties,[31] but markedly decreased the electrical conductivity of the refined aluminum.[32] An increase of 0.005 per cent titanium increased the electrical resistivity 0.00016 ohms per square millimeter per meter.[33] The mechanical properties were slightly affected. According to Stroup,[34] the electrical conductivity of aluminum was increased by alloying 0.01 to 0.5 per cent boron in the presence of up to 1.0 per cent titanium. The solubility of hydrogen was increased noticeably by the addition of titanium.[35] Very small proportions increased the impact resistance and tensile strength, but amounts above 0.19 per cent had an adverse effect. Both the Erichsen value and electrical conductivity were markedly decreased by very small percentages.[36] Optimum mechanical properties were obtained with 0.5 to 1.0 per cent, and at the same time resistance to the action of organic acids, saline solutions,[37] and zeolite water[38] was improved. Seasonal cracking of high tensile strength aluminum alloys was greatly reduced by adding titanium to prevent intercrystalline corrosion.[39] Such an alloy, containing 0.5 per cent of this constituent, was heat-treated.[40] A titanium content of more than 20 per cent increased the hardness of the product, but more than 37.3 per cent resulted in the formation of a nonhomogeneous mass containing undecomposed salts. The compound Al_3Ti resulted, but there was no indication that it formed mixed crystals with the aluminum. No other compound was detected.[41]

Addition of titanium gave improved castings, but sharp corners and too great wall thickness were avoided.[42] In amounts up to 0.2 per cent it tended to induce a finely grained structure[43] and allowed a lower casting temperature.[44] In aluminum alloy castings containing 6 per cent iron, it changed the macrostructure and facilitated working under pressure.[45] An adherent coating of an aluminum alloy

containing zinc and titanium improved the corrosion resistance of aluminum-base alloys.[46] The coating was applied by casting, welding, atomizing, or electroplating.

Ferran[47] studied the optical characteristics of aluminum-titanium alloys.

Titanium improved the stress-corrosion behavior of aluminum-magnesium-zinc alloys,[48] but increased the rate of corrosion in water.[49] Small additions resulted in fine crystals of aluminum-silicon alloys after heat treatment,[50] and decreased the solid solubility of copper and magnesium in aluminum, as well as the hardness of the alloy.[51] An aluminum alloy containing small proportions of titanium, copper, tin, zinc, magnesium, and chromium required no heat treatment and possessed special machining qualities.[52] Aluminum alloys containing manganese and titanium in the as-cast condition have been reported to rival in strength and durability the strongest alloys without such additions, even after heat treatment.[53] In Germany during World War II, titanium was used as a constituent of light-metal alloys free of strategic materials, for making pistons.[54]

The titanium content of aluminum or its alloys was reduced by introducing into the molten bath a mixture of nitrogen and chlorine, and skimming off the resulting dross of nitride compound.[55] Chlorine could be replaced by readily decomposing halogen compounds. In a related method,[56] the molten metal was treated with an alkaline earth metal or magnesium in an amount corresponding to the titanium content, and, on cooling to a point just above the solidification point of the mass, a sediment rich in titanium was obtained.

Borgnis[57] prepared alloys free from copper, iron, metalloids, and all volatile materials by the reaction between approximately equal parts of titanium dioxide and granulated aluminum, initiated with a very small amount of zinc chloride.

The addition of 0.4 per cent titanium increased the tensile strength of aluminum alloys containing 8 per cent magnesium.[58] In duraluminum-type alloys it decreased the grain size in the primary recrystalline zone,[59] although in the secondary zone proportions up to 0.3 per cent resulted in a coarser grain, and 0.5 to 1.7 per cent decreased the size. Titanium was effective in refining the grain of duraluminum slabs and in retarding age hardening.[60] Gauthier[61] reported that an addition of 0.02 per cent at each remelting of such an alloy, containing 0.02 per cent beryllium, fully compensated the action of the latter metal in increasing the grain size, and gave su-

perior castings because of improved resistance to oxidation in the molten state and in the presence of moist molding sand. These alloys were suitable for use in machines for casting under pressure. Beryllium in amounts of 0.005 to 0.5 per cent produced a large increase in corrosion resistance of magnesium, but the concurrent tendency to yield larger crystals was counteracted by adding titanium.[62]

Refinement of grain of worked aluminum bronze 6 to 8 per cent was effected by similar additions.[63] Such alloys could be cold-rolled to 60 per cent reduction and annealed at 700° to 800° C. According to Nishimura,[64] in normal amounts (0.02 to 0.46 per cent) it did not decrease the hardness of aluminum-copper alloys at high temperature. In light alloys containing nickel, from 0.05 to 0.50 per cent acted as a refining agent during melting and solidification.[65] It decreased the size of primary crystals, made heat treatment easier, and reduced the tendency of the aluminum to oxidize.

An aluminum-base alloy for filling teeth contained 0.08 per cent titanium, 0.19 per cent silicon, 0.25 per cent copper, a trace of zinc, and up to 4 per cent iron.[66] Another alloy, containing up to 1 per cent titanium, was suitable for wrought parts of internal-combustion engines.[67] Textile machinery made of such an alloy, containing 0.15 per cent titanium, reduced the blackening of textiles during processing.[68] An aluminum-alloy disk for sound recording contained 0.01 to 0.3 per cent.[69]

Miscellaneous

Titanium is used in copper-nickel and cobalt-zinc solders.[70] Alloys of titanium-beryllium-nickel with cobalt, molybdenum, and iron have high strength and are highly resistant to mineral acids, alkalies, and organic materials.[71] Up to 5 per cent titanium has been employed in alloys for electrical resistance units; a typical composition contained 6 to 30 per cent chromium, 3 to 12 per cent aluminum, 0.07 to 0.20 per cent carbon, and 5 per cent titanium.[72] An alloy for casting dentures contained cobalt, together with titanium 1 to 30 per cent, chromium 3 to 45 per cent, and beryllium 0.5 to 15 per cent.[73]

By the aluminothermic process, Honingschmid[74] prepared titanium silicide, $TiSi_2$. Phosphidic alloys resistant to corrosion contained 35 to 71 per cent iron, 1.7 to 25 per cent phosphorus, and 6 to 37 per cent nickel, with 5 to 25 per cent titanium to form phosphides and alloy with the nickel and with iron phosphides.[75]

Alloys of titanium with iron, chromium, magnesium, nickel, copper, and cobalt were produced by electrolyzing a fused titanium salt with a cathode of the base metal.[76] A current density of 18 to 30 amperes per square centimeter at the cathode and 0.8 to 1.2 amperes per square centimeter at the anode was used.

Titanium has been employed in magnesium alloys for casting and rolling,[77] and for machine parts.[78] Such alloys have good ductility.

The solubility of titanium in zinc was extremely small. An eutectic formed at 418° C. which contained only 0.15 per cent titanium.[79] Such alloys could be rolled,[80] and titanium increased the retention of impact strength during prolonged heating.[81] In proportions up to 1.6 per cent it imparted high creep resistance.[82]

Very pure alloys free from carbon were produced by dissolving titanium dioxide in molten electrolytic manganese, adding metallic aluminum to reduce the titanium dioxide and removing part of the manganese by distillation.[83] Wallbaum[84] carried out X-ray examinations of such alloys and determined the physical constants of the compound Mn_2Ti.

Udy[85] heated a mixture of finely divided titanium dioxide and calcium oxide to effect chemical combination, and reduced the product with a noncarbonaceous agent to form alloys.

Alloys of gold with titanium have been recommended for the construction of resistance manometers.[86] Titanium alloys containing 10 to 60 per cent tantalum, columbium, molybdenum, tungsten, zirconium, or vanadium were resistant to corrosion and had high optical reflectance.[87]

Permanent Magnets

Titanium is employed as an important constituent of alloys used for making permanent magnets. Such an alloy, composed of 11 per cent titanium, 16 per cent nickel, 28 per cent cobalt, and 45 per cent iron, had a residual magnetic inductance of 7500 gauss and a coercive force of 830, and retained its magnetic properties over a wide temperature range.[88] Magnets having a B. H. maximum of 1,000,-000 or over and a coercive force of 500 or over were prepared from a heat-treated alloy containing iron as the major constituent, along with 30 to 35 per cent nickel, 10 to 15 per cent aluminum, and 0.4 to 4 per cent titanium.[89] The material was first heated to 1100° to 1300° C. and quenched in oil, after which it was reheated to 675° to 775° C. and cooled in air. A similar alloy, produced by Honda,[90] contained up to 50 per cent titanium, with 3 to 50 per cent nickel

and at least 20 per cent iron. A large part of the nickel could be replaced by cobalt without affecting the properties. Aluminum was employed in some compositions, and a specific alloy of this type contained 35 per cent cobalt, 18 per cent nickel, 8 per cent titanium, 6 per cent aluminum, and 33 per cent iron. Others consisted of 30 to 36 per cent cobalt, 16 to 25 per cent nickel, 6 to 12 per cent titanium, 6 to 11 per cent aluminum, and the remainder iron.

An alloy of nickel, iron, chromium, and titanium has been employed for parts requiring a very constant permeability in weak magnetic fields, and at the same time a high electrical resistance.[91] Magnetic alloys suitable for telephone and telegraph apparatus contained 10 to 60 per cent iron, 40 to 90 per cent nickel, 0.1 to 5.0 per cent tin, 5.0 per cent chromium, and up to 2.0 per cent titanium.[92] Polzguter [93] recommended an alloy containing iron, together with 30 to 36 per cent cobalt, 16 to 20 per cent nickel, 6 to 8 per cent titanium, and aluminum in an amount above 70 per cent of the titanium. Many modifications of the composition and method of preparation of titanium containing alloys of this type have been reported.[94]

In the manufacture of permanent magnets from alloys of this type containing from 3 to 15 per cent titanium, the mass was quenched from 1000° to 1300° C. into a bath at 550° to 750° C., and slowly cooled to room temperature.[95] The product was then aged at 650° to 680° C., and again cooled to room temperature.

Permanent magnets made from metal powders and a synthetic resin binder were 20 per cent as efficient as cast magnets, but were less brittle and more adaptable to mass production.[96]

Chapter 23

HARD ALLOYS

Titanium forms a series of extremely hard metal-like compounds with carbon, silicon, nitrogen, and boron which are used in a number of fused or sintered alloys and in abrasives. Typical applications are in tips for cutting tools and dies and in abrasive stones and wheels.

Carbide

Of these, the carbide is more important commercially, and because of its extreme hardness and low manufacturing cost it has many applications as an active component of hard alloys for the manufacture of such articles as tips for cutting tools and dies and as an abrasive, both as a loose powder and cemented into stones. Usually the compound is employed in association with other carbides, particularly those of tungsten, molybdenum, and vanadium. For example, tools containing titanium carbide are better for cutting steel but less effective for cutting cast metals or others giving short chips.[1] Titanium carbide is harder than tungsten carbide, but has a lower heat conductivity, so that for cutting steel the higher hardness is more important, although it is of no appreciable advantage in cutting the relatively soft cast iron, and in fact the lower thermal conductivity causes more rapid wear of the tool. According to Dawihl,[2] the extraordinarily high wear resistance of carbide materials results from their relatively small deformability and from their ability to retain the high degree of hardness at elevated temperatures.

To produce hard shaped articles, the titanium carbide may be heated directly to fusion and cast in carbon molds, or it may be ground, mixed with a powdered metal of the iron group as binder, pressed into shape, and consolidated by heating at a high temperature, 1300° to 2500° C.[3] From 1 to 25 per cent of the binding agent may be incorporated in the hard alloy, but, in general, 5 to 10 per cent gives optimum results. Petersson[4] heated such a mixture in a mold to 1500° to 2500° C. and cooled the shaped product under a pressure of 1 to 3 tons per square inch. Up to 5 per cent thorium oxide prevented rapid crystal growth at the high tempera-

ture. A series of heating and pressure cooling steps were sometimes required. Ollier [5] ball-milled a mixture of 3 per cent powdered cobalt or nickel with sized titanium carbide to coat the carbide particles, then added 3 to 7 per cent of an equal mixture of sponge iron and steel, again milled, pressed the composition into the desired shape, and sintered. Five per cent titanium hydride, which liberated hydrogen slowly at 680° F., mixed with the metal powders increased the compact density of the alloy by reducing oxides during sintering.[6] An externally supplied reducing atmosphere was not necessary, and the sintering time was reduced appreciably. Instead of employing metals of the iron group alone as sintering agents, better bonds were reported by using alloys of one of these metals with tungsten, molybdenum, or chromium,[7] or silver alloys containing cadmium, zinc, and magnesium.[8] Ridgway [9] mixed fused granular titanium dioxide with the required amount of carbon and heated the mixture about an electric-furnace resister, out of contact with oxygen and nitrogen, to form a titanium carbide ingot suitable for crushing. Titanium carbide alone or mixed with tungsten carbide was produced by reducing the corresponding oxides with carbon, and from this product hard sintered alloys were formed containing 7 to 15 per cent titanium carbide, 3 to 14 per cent cobalt, and the rest tungsten carbide.[10] Schwartzkopf [11] mixed finely divided titanium carbide with metallic tungsten and carbon, and heated the mixture to 1600° to 2600° F. to form tungsten carbide and produce solid solution. Similarly, tungsten carbide was mixed with metallic titanium and the stoichiometric equivalent of carbon, and the composition was heated to cause reaction.[12] According to another modification, titanium dioxide was heated with carbon in an atmosphere of nitrogen to produce the nitride, which was heated with tungsten carbide and carbon to form a solid solution of the two metallic carbides.[13] By a similar process, titanium dioxide was heated to incandescence with an excess of carbon black, tungsten or molybdenum was then added, and the mixture was heated to 1400° to 1800° C.[14] To produce dense and tough hard alloys, powdered tungsten carbide or molybdenum carbide was mixed with powdered titanium carbide, heated to 1500° to 2000° C., comminuted and mixed with 5 to 20 per cent of a metal of the iron group and 1 to 2 per cent of a volatile binder, again heated to facilitate shaping and to drive off the volatile components of the binder, and finally sintered at 1400° to 1600° C.[15]

Burow [16] sintered a mixture of finely divided carbide of titanium with powdered iron, nickel, or cobalt and 0.1 to 2.0 per cent silicon.

Such a mixture was pressed into shape and sintered in hydrogen to prevent reaction of the constituents of the atmosphere.[17] Carbides, borides, nitrides, and silicides fused in an atmosphere of hydrogen were cemented in heating a mixture of the finely divided material with a powdered metal of the iron group, in a refractory mold, to a temperature above the melting point of the bonding materials.[18] A dense nonmetallic article, consisting of particles of titanium carbide alone or mixed with other hard carbides embedded in a matrix of boron carbide, in which a portion of the grain material was dissolved, was produced by heating the mixture at a temperature short of complete fusion but sufficient to produce the desired plasticity.[19] The addition of 5 to 10 per cent titanium carbide to a silicon carbide-boron carbide article minimized the tendency to crack during formation and cooling. A mixture of 70 per cent tungsten carbide, 15 per cent tantalum carbide, and 15 per cent titanium carbide was pressed and sintered at 1400° to 1700° C. to form a hard alloy without an auxiliary bonding metal.[20]

A product in which the titanium carbide was absorbed to form monophased mixed crystals in solid solution was reported to have increased strength and toughness.[21]

The highest saturation of titanium carbide with carbon was obtained by heating a mixture of titanium dioxide and lampblack in an atmosphere of hydrogen to a maximum temperature without prolonged exposure.[22] X-ray studies showed that titanium carbide produced in an atmosphere of hydrogen or in vacuum was deficient in carbon, but that it contained sufficient oxygen and nitrogen to fill all places in the crystal lattice.[23] Examinations with X rays of fused and sintered mixtures of titanium carbide and tungsten carbide in various proportions showed no evidence of the formation of the double carbide compound, $W_2Ti_2C_4$.[24] On increasing the temperature from 1500° to 2700° F., the amount of tungsten carbide in the homogeneous phase increased from 44.0 to 91.8 per cent. Metcalfe[25] investigated the structure and lattice parameters of the alloys of titanium carbide and tungsten carbide by X-ray powder diffraction method. The solid solubility of titanium carbide in tungsten carbide was low even at temperatures around 2500° C., but titanium carbide dissolved in tungsten carbide 73 per cent at 1400° C., 82 per cent at 2000° C., and increased to a maximum of 95.5 per cent at 2450° C. Intensity measurements on the films showed that the structure of this solid solution consisted of a random distribution of the metal atoms in the face-centered cubic positions, with carbon atoms octahedrally coordinated. The investiga-

tion was extended to 2800° C. and equilibrium diagrams were drawn.

To produce titanium carbide free from graphite the impure product was heated with manganese to form Mn_3C, which was later leached out with dilute acid.[26] Free carbon was removed from carbides, cyanonitrides, and carboxides of titanium by agitating the crude material in a finely divided state with 0.1 to 1.5 per cent aqueous soap solution.[27]

Uhlmann[28] pressed a mixture of titanium powder and carbon into shape and exposed it in an atmosphere of coal gas or a stream of oil vapor, carbon monoxide, and methane to the action of a high-frequency electric field. According to another modification, an ore of titanium was subjected to a reducing operation in admixture with a sufficient amount of iron and an excess of coke or charcoal to obtain an impure alloy containing iron and titanium carbide.[29] This product was subjected to a further treatment to separate the carbides. Iron could be initially present as oxide.

The best fine-grained carbide was reported to be made by exposing a mixture of the titanium dioxide, with carbon, in an atmosphere of hydrogen at 1900° C. for a short time.[30] Carbon diffused into the solid phase rapidly at this temperature. Direct production of a fine powder suitable for the preparation of cutting compositions without crushing was effected by heating titanium dioxide in an intimate mixture with coal, or in a carbonizing atmosphere, to a temperature just below the fusion point of the carbide.[31] An intimate mixture of a metal of high melting point, such as tungsten, and oxides of a metal of still higher melting point and more tenacious, such as titanium, and an amount of coke necessary to form the carbides, was shaped, heated to 1500° C. to reduce the oxide, and then to a higher temperature to complete the carburization.[32] Carbides in the proper proportions for forming hard alloys may be produced directly from mixtures of the metals titanium, tungsten, and vanadium.[33]

Such an alloy, prepared by sintering at 1500° C. a shaped mixture of titanium and tungsten carbides and metallic cobalt as a binder, had a hardness of 87 to 90 on the Rockwell C scale.[34] In general the hardness of these materials increased with decreasing grain size of the carbides, but there was a practical limit to the degree of subdivision because of the formation of larger crystallites during the sintering operation. Large grain sizes required higher pressure and temperature in the cementing operation. Curves of the relationship of hardness against pressure, and against temperature

of sintering, showed maxima.[35] Iron and cobalt metals, and alloys of cobalt and tungsten and of iron and tungsten, were successfully employed as bonding agents.

Sintered compositions containing 30 to 50 per cent metals of the iron group, 2 to 10 per cent chromium, and the remainder carbides of titanium and tungsten in the ratio of 1 part of the former to form 0.5 to 2 parts of the latter could be hardened by heating to 1000° to 1200° C. and quenching in oil.[36]

Nitride, Boride, and Silicide

Previously sintered titanium dioxide was powdered, shaped with an organic binder, and heated strongly in ammonia to produce strong articles of titanium nitride.[37] Alternatively, the titania was formed into a solid mass, sintered, and converted to a nitride by strong heating in an atmosphere of ammonia or other nitrogenous gas. A finely ground mixture of equal parts of titanium nitride and carbide, with 7 to 10 per cent cobalt, was pressed into shape and sintered at 2400° F. on a carbon bed in an atmosphere of nitrogen to form a hard alloy for cutting tools.[38] Another composition of similar properties consisted of titanium nitride in admixture with vanadium nitride or boride.[39] Fritted or fused mixtures of titanium nitride and carbide, containing up to 25 per cent auxiliary bonding metal, have been used for cutting tools,[40] and a mixture of 10 per cent titanium nitride, boride, or silicide, along with 85 per cent tungsten carbide and 5 per cent cobalt as bonding agent, had very desirable properties for this purpose.[41]

Hard sintered alloys containing a major proportion of titanium boride or silicide and a minor proportion of the carbide, with 0.5 to 25 per cent of a metal of the iron group as cementing material, have been employed in making cutting tools.[42] Typical compositions represented titanium boride 75, titanium carbide 20, and nickel 5 per cent; titanium silicide 55, tungsten carbide 33, and nickel 12 per cent; and titanium boride 50 or more per cent along with carbides of tungsten, molybdenum, or titanium, and 1 to 25 per cent metallic iron, cobalt, nickel, or manganese.[43] Such hard compositions were made from titanium boride, together with a separate crystalline phase of titanium carbide solidified from a fused mass.[44] Hinnuber[45] prepared hard sintered alloys of titanium boride and nitride; a representative product consisted of 34 per cent titanium nitride, 60 per cent titanium boride, and 6 per cent nickel. Tools and dies adapted for drawing wires have been formed of titanium

metal, the outside shell of which was converted to the boride or carbide to obtain the desired hardness.[46]

The resistance and tenacity of carbides, nitrides, borides, and silicides of titanium were improved by heating the materials before and after reaction at 3400° to 3600° C. in the presence of atomic hydrogen.[47]

Cutting Tools

Many hard-alloy compositions (consisting primarily of titanium carbide and tungsten carbide), suitable for making tools and dies have been reported, and a few are given below as representative of the group: a major proportion of titanium and tungsten carbides with zirconium carbide and cadmium carbide compressed and fritted in an inert atmosphere at 1600° C.;[48] 30 to 60 per cent of metals of the iron group or their ores, 5 to 30 per cent chromium, 15 to 50 per cent tungsten or molybdenum, 15 to 50 per cent titanium and 1 to 3 per cent carbon;[49] 60 per cent tantalum carbide, 5 per cent titanium carbide, 11 per cent columbium carbide, 20 per cent tungsten carbide, and 4 per cent cobalt carbide;[50] 35 to 80 per cent tungsten carbide, 5 to 45 per cent tantalum carbide, 0.5 to 30 per cent titanium carbide, and 5 to 15 per cent iron, cobalt, or nickel as binding agent;[51] other alloys with carbides of tungsten, tantalum, and molybdenum as the major component, contained 5 to 33 per cent titanium carbide and a metal of the iron group as bonding agent.[52]

Tools for the rapid machining of steel were made from a sintered composition of tungsten carbide with titanium carbide and nitride, and a binder alloy of a metal of the iron group and tungsten.[53] The weight of tungsten carbide was 10 times the combined titanium nitride and carbide, the ratio of the latter two constituents was not more than 1 to 5. A similar product of tungsten carbide with 16 per cent titanium carbide and 1 per cent vanadium carbide, with 5.5 per cent cobalt as bonding agent, had a high efficiency in machining steel.[54]

In making cutting tools, finely divided metallic titanium was mixed with powdered iron, cobalt, nickel, manganese, or copper, sintered, alloyed, and then carburized.[55] The finely divided product was mixed with aqueous ammonia starch paste, extruded into stock shapes, dried, cut into the desired sizes and shapes, carburized, and bonded at a temperature just below the melting point of the base metal to effect cementation.

Various proportions of titanium carbide and tungsten carbide,

together with smaller proportions of other carbides cemented with iron or other bonding agent, have been employed in producing high-speed cutting tools.[56] Similar compositions have been used for making wire-drawing dies and electrical contact points.[57]

In producing tools of hard alloys, the mass was surrounded with loose particles of carbides, such as titanium, of such size as to permit free flow of gas through their interstices.[58]

Before attaching a titanium carbide alloy to a metal base in forming cutting tools, better results were reported if the surface of contact was first fluxed and a brazing alloy consisting of 40 to 90 per cent copper, 5 to 30 per cent chromium, and 5 to 30 per cent cobalt or iron was interposed.[59] The brazing alloy was melted and the titanium carbide composition was maintained in position on the base until the alloy solidified.

Such a hard resistant alloy, adapted to be welded directly upon a steel tool shank for use as drilling or mining tools, contained over 50 per cent tungsten or molybdenum, 2 to 6 per cent titanium, 25 to 34 per cent of a metal of the iron group, 10 to 15 per cent chromium, and sufficient carbon to form carbides with the tungsten, molybdenum, and titanium.[60] A composition consisting of titanium and tungsten carbides, cemented with a metal of the iron group, has been applied to the surface of rolling-mill rolls to increase the hardness and diminish wear.[61] For producing a surface of great hardness and resistance to wear on a softer core material, titanium metal in finely divided form was applied to a mold and carburized. The resulting carbide was fused and the carrier metal was cast into the shell to form the remainder of the article.[62] In a similar application, a hard alloy of titanium, tungsten, and other carbides, cemented with iron, was made into a welding rod, and this was fused and allowed to drop onto the softer metal to be coated.[63]

Titanium carbide has been added to the matrix in which diamonds are set in drills for the purpose of hardening.[64] The compressed alloy obtained from a mixture of 20 per cent titanium carbide, 72 to 78 per cent tungsten carbide, and 2 to 8 per cent nickel or cobalt has been used for making pivots for escapements and similar parts of watches.[65] Sheets, strips, and wires were produced by mechanical treatment from a compressed, sintered mixture of 1 to 5 per cent titanium carbide, 25 to 40 per cent iron, nickel, or cobalt, and the remainder, carbide of tungsten or molybdenum.[66]

A hard, intermetallic, crystalline compound, corresponding to the formula $WTiC_2$, was formed by heating a mixture of tungsten, titanium, and carbon for a prolonged period in a bath of molten

nickel above 2000° C. in a graphite crucible.[67] On cooling the com-
pound was separated from the nickel by digestion, first with aqua
regia and finally with hydrofluoric acid. The crystals had a hard-
ness of 9.8 on the Mohs scale.

Its principal application is in a series of hard alloys, known com-
mercially as "Kennametal," which vary in hardness from 89 to 91
Rockwell "A" and have strengths of 200,000 to 300,000 pounds
per square inch, transverse-rupture test. The modulus of elasticity,
50,000,000 pounds per square inch, is about twice that of steel but
less than that of cemented tungsten carbide, which is 80,000,000.
Thus such products are less rigid but capable of withstanding more
shock without breaking. These alloys are produced in vacuum
furnaces by processes of powder metallurgy and are high-priced,
so that they are used chiefly in small articles such as tool points, die
inserts, and valve inserts weighing less than 100 g. In making
lathe tools, blanks of the hard alloys are brazed into recesses in steel
shanks with silver solder, bronze, or copper; die or nozzle inserts
may be shrunk in place. Grinding of cutting tools is done with
loose-textured wheels of silicon carbide or diamond dust, bonded
with bakelite. Valve balls, nozzles, and dies are made by lapping
with diamond dust. Cutting tools of these alloys have a finer grain
structure, since the compound is not subject to grain growth and
subsequent weakness during heat treatment. Consequently they are
used chiefly for working stainless and hard alloy steels and monel
metal.

In preparing cutting tools, the carbide particles and metallic
binder were mixed in a liquid hydrocarbon, dried, and molded into
shape under pressure before sintering.[68] The shaped article was
heated in the presence of magnesium as a reducing agent, under
subatmospheric pressure, at a temperature sufficient to cause the
binder to flow.

Abrasives

Grinding wheels may be made by firing a mass of abrasive grains,
such as titanium carbide, nitride, silicide, or boride, with a vitrefi-
able ceramic bonding material such as fusible clay.[69] A recom-
mended abrasive consists of a fused mixture of boron carbide, as a
major constituent, along with titanium carbide.[70] Abrasive grains
may be bonded into wheels or other forms with the thermal reac-
tion product of an alkali metal silicate and a modifier consisting of
titanium dioxide, zinc oxide, and pulverized flint.[71] Titanium sili-
cide has been suggested as a polishing agent for precious stones.

Chapter 24

ELECTRICAL INDUSTRY

Lamps

Around the turn of the century, considerable interest was aroused in the use of titanium and its compounds in the production of arc lamp electrodes, incandescent filaments, and gas mantles, and much research was devoted to the development of the various types of light elements. At the present time, however, interest seems to have largely subsided, but it may be revived because of the inherent possibilities of titanium in this field, particularly in arc lamps. The more important properties in this connection are high fusion and vaporization temperatures and high radiation efficiency. Titanium gives one of the richest spectra of any of the elements so far as number of lines is concerned, and it decreases the tendency of the arc to sputter and flicker. One disadvantage is its comparatively low electrical conductivity. As early as 1878 Edison obtained a patent in England for an arc lamp electrode containing rutile, but the first United States patent mentioning the application of any compound of titanium for this purpose dates from 1890.[1] Titanic acid was added to the carbon used in making the electrodes to improve the steadiness and intensity of the light.

Rutile was extensively used in the manufacture of the cathodes of magnetic arc lamps, which also contained magnetite and chromite. The magnetite particles made the arc stream a good conductor, while the incandescent particles of titanium dioxide, carried into the arc by the electric current, were responsible for most of the luminescence. Chromite was added to increase the life of the electrode. The iron oxide also contributed conductivity to the cold electrode, as the other oxides were conductors only while hot.

Electrodes of titanium-iron alloys were reported to give a brilliant yellow light and to have greater durability and current efficiency. Titanium carbide has been employed as the luminous core of arc lamp electrodes. In one case the carbide was surrounded with an iron tube, and in another it was plated with copper to increase the electrical conductivity and prevent oxidation during the opera-

447

tion of the lamp. Such an electrode permitted a longer arc to be drawn and was almost free from hissing and decrepitation. By incorporating a small amount of chromium carbide with the titanium carbide, the life of the electrode was increased without diminishing the illuminating power.

Titanium suboxide, prepared by the partial reduction of rutile, has also been used in making electrodes, but as with the carbide better results were obtained by employing these as the positive element along with a negative electrode of a better conducting material, such as copper or graphite.[2] With both the carbide and the suboxide it was necessary to employ a special starting device, as a nonconducting layer of titanium dioxide tends to form at the tips of the electrodes on cooling. The grayish product obtained by heating rutile to 800° to 1000° C. in a reducing atmosphere was used for electrodes, conductors, and containers.[3] An anode for producing an intense arc with Beck effect has an outer shell of carbon, an intermediate shell of cerium fluoride or other rare earth compound, and an innermost core containing titania to correct the color of the flame.[4] An incandescible body of titanium dioxide, comprising a rare oxidizable metallic oxide conductor at ordinary temperature, was employed in an atmosphere of an inert gas with a small amount of oxygen sufficient to cause the material to retain its electronic condition at a temperature of around 2000° C. but insufficient to cause conversion of the oxide to the higher form in which it would become nonconductive.[5] In a composite lamp, a metal unit had bonded to it a lead glass, and to the glass there was fusion-welded a joint of ceramic material fired at an elevated temperature and composed of 0.5 to 2 parts titanium dioxide, 65 to 80 parts magnesium oxide, and 20 to 35 parts beryllium oxide.[6]

According to Weedon,[7] of the many substances investigated for possible use in arc light electrodes, those containing titanium gave the highest efficiency in candle power per watt consumed.

A unique arc lamp described by Darrah,[8] in which the supply of material for the arc did not come from the electrodes but from a surrounding gas or vapor, gave particularly good luminous effects. The two electrodes made of tungsten were enclosed in a heat-resisting glass bulb filled with titanium tetrachloride or the mixed dichloride dibromide, and since the supply of material came from the surrounding vapor rather than from the electrodes, the lamp required little more attention than one of the incandescent tungsten type.

Titanium filaments were tried out in incandescent electric lamps, and some were reported to have been placed on the market around 1913, but because of difficulties in producing the pure metal and drawing it into wire, and because of its tendency to combine with oxygen and nitrogen, the manufacture of these lamps was never extensive and was soon discontinued.[9] Rather than drawing the titanium, it was ground to a fine powder in the absence of oxygen, worked up into filaments and rods by pressure, and ignited in an atmosphere of hydrogen to effect solidification.[10] With the commercial production of malleable and ductile titanium metal in 1948, it seems probable that its use in electric-light filaments will be revived. The pure metal in the form of rods is employed to produce spectra for astronomical research.

A fused mixture of titanium dioxide, magnesium oxide, and beryllium oxide has been employed as the fluorescent material in lamps.[11] The light emitted is in the red spectral region.

The interior of tungsten filament electric light bulbs is coated with fumes of the oxides of titanium produced by burning the metal.[12]

Oxides of titanium were found to be unsuited for use as constituents of Welsbach gas mantles.[13]

Electron Discharge Tubes

Small proportions of titanium (0.25 per cent or more) have been employed in nickel and cobalt alloys for cathodes of electron discharge devices [14] and for electrodes and other metal parts of thermionic valves.[15] A manganese-activated beryllium germanate of titanium may be employed as the luminescent material for use in cathode-ray tubes.[16] Granular semiconducting materials, such as the carbide, boride, nitride, or silicide of titanium, have been found suitable as the carrier for the emitting layer of alkali or alkaline earth metal of the cathode of discharge apparatus.[17]

Thermionic cathodes of nickel and cobalt wire have been treated with titanium.[18] A metal filament was supported by lead-in wires, and one or more eyelets, consisting of a metal core wire of molybdenum or tungsten carrying a coating of nitride or carbide of titanium.[19] In a similar electric discharge tube, one or more of the electrodes were coated with black titanium oxide.[20] Titanium dioxide was applied to the supporting member made of tungsten, molybdenum, iron, and nickel, and reduced by heating in vacuum at

1500° C. If other metals were used for support, the titanic oxide was reduced by heating in the presence of hydrogen or a mixture with nitrogen. Such a nonemitting electrode was used in envelope with a cathode. Titanium has been used as getters in electronic lamps to absorb hydrogen,[21] and in radio tubes to remove the last traces of oxygen and nitrogen. In designing a discharge tube containing a secondary emission electrode of a titanium compound, means were provided for introducing a chemical agent capable of converting any objectionable free metal deposited on the electrode during operation.[22] An insulating wall of titanium dioxide and quartz or alumina was applied to a conducting core of a lower oxide in an electron discharge device.[23] An oxyacid of nitrogen (nitric acid) was used with powdered titanium, as well as other metals, to form a tacky composition as an insulating material for the parts of such tubes.[24] An insulating film was formed on an electrically conducting surface by evaporating titanium borate onto the surface in vacuo.[25] Applications of the process were made in the manufacture of mosaic electrode for use in a cathode-ray tube.

Titanium monoxide, TiO, seems very promising in electronics, since it is a semiconductor and amplifier. It is used in powerful midget tubes which may make possible extremely small radio and television sets.

Thermocouples

Thermocouples of relatively high efficiency can be prepared, using as the negative element an alloy of 91 per cent nickel and 9 per cent titanium and as the positive element an alloy of copper and nickel.[26] The titanium alloy was ductile and resisted oxidation at high temperatures. Both elements had a small thermal conductivity and a low temperature coefficient. The thermal electromotive force of such a couple was 0.09 millivolts per degree Centigrade.

Resistance Heating Units

Electrical resistance heaters, made of tantalum carbide as the principal component, may contain 8 to 30 per cent titanium.[27] An ignition electrode, to be permanently immersed in the liquid cathode, was composed mainly or wholly of titanium dioxide with one or more of the oxides of barium, strontium, or calcium.[28] In forming the product a mixture of the oxides was heated for 30 to 60 minutes at 1500° to 1800° C. in an atmosphere of hydrogen. Electric contacts resistant to oxidation were formed of 50 to 99 per cent nitrides

of titanium, together with 1 to 50 per cent of gold, silver, or copper, or their alloys.[29] Electrical heating elements consisting of a metallic conductor and a casing of ceramic material were improved by placing between the two units materials capable of combining with oxygen, such as nitrides, carbides, or hydrides of titanium.[30] A protective coating of a sintered mixture of titanium dioxide, silica, chromic oxide, and alumina was used to prevent oxidation of an electric heating unit of high melting point, such as molybdenum, tantalum, and tungsten.[31] Wejnarth[32] found that silicon carbide electrical resistance units could be made more resistant to corrosion at high temperature by incorporation of a small proportion of titanium carbide or nitride. Ridgway[33] produced electric furnace resistor rods by crystallization from a fused mass containing at least 95 per cent titanium dioxide.

To study the mechanism of current rectification at the boundary of a semiconducting layer (titanium dioxide) on a metal, Ioffe[34] investigated the contact resistance and potential of the semiconductor. A considerable added resistance was observed near the contact where the titanium dioxide joined a metal possessing a higher contact potential or bordered on a metal having a lower contact potential.

Insulators of borosilicate glass have been made with an electrically conducting iridized zone of tin oxide and an overlying nonconducting iridized coating of titanium dioxide.[35] The surface of etched electrodes for electrolytic condensers can be cleaned by adding colloidal titanium dioxide to absorb the etching agent, such as hydrochloric acid or resulting chlorides.[36]

Insulators

Since titanium dioxide has good dielectric properties, it is employed as a major constituent of sintered ceramic and organic bonded electrical insulating materials of various types.

A product of small dielectric losses at all frequencies was produced by sintering a mixture containing at least 70 per cent titanium dioxide with oxides of tungsten or molybdenum, and using china clay or an alkaline earth metal oxide as plasticizing agent.[37] According to other modifications, a mixture of titanium dioxide with an alkali or alkaline earth metal halide and an oxide of copper, zinc, or barium was molded into the desired shape and fired at Segar cone 12 to 15 to produce a composition having a high dielectric constant;[38] a mixture of titanium dioxide with 0.5 to 10.0 per cent of

a water-soluble inorganic sulfate or phosphate was heated at 1200° C.[39] Improved dielectric properties were developed by firing the ceramic mixture, consisting mainly of titanium dioxide, in an oxygen-rich atmosphere,[40] or by allowing the fused mixture to cool in an electric field to effect orientation of the growing crystals.[41] The dielectric constant of high titanium dioxide products of this type was practically unaffected by frequency from 60 to 1,000,000 cycles.[42] X-ray studies showed the formation of rutile crystals. A fused mixture, consisting of titanium dioxide as the main component, together with minor proportions of oxides of hafnium, cerium, or thorium, or a mixture of these, has been recommended as an electrical insulator.[43]

Suzuki[44] made insulator porcelains by firing at 1300° to 1410° C. a mixture of 25 to 40 per cent alumina, 25 to 33 per cent silica, 10 to 60 per cent titania, 0.5 to 3 per cent alkali metal oxide, and 0.5 to 6 per cent alkaline earth metal oxide. If the content of alumina was less than that of silica, the proportion of titanium dioxide was increased. Reduction was avoided as much as possible during the sintering operation. Steatite porcelains,[45] produced by firing a mixture of titanium dioxide, Korean kaolin, talc, limestone, and quartz at 1300° to 1380° C., were found to be suitable as insulation for high-frequency currents. A similar composition[46] in which the magnesia was replaced by lime and the silica by titanium dioxide yielded insulators having high dielectric constant and low power coefficient, well suited for high-frequency applications.

Condenser Dielectrics

A material of high specific inductive capacity, suitable for condenser dielectrics,[47] was prepared by heating preroasted titanium dioxide with clay and sodium titanium silicate to form a cemented mass. Products of similar electrical properties were prepared by bonding particles of titanium dioxide with an alkali-free titania glass or calcium titanium silicate.[48] The sintering agent could also contain magnesium or beryllium oxides. Clayey substances alone served as the bonding agent.[49] Rath and Handrek[50] deposited chemically precipitated titanium soap upon a suspension of titanium dioxide, separated the solid mix, pressed it into forms suitable for condenser dielectrics, and sintered to a solid mass. Dielectrics for heavy condensers were prepared from mixtures of titanium dioxide with 5 to 10 per cent zirconium oxide.[51] Such products had a dielec-

tric constant of 80 to 90 and a loss factor of 10 to 20×10^{-4}. According to Kamayachi and Sugiura,[52] the best titanium dioxide condenser porcelain was baked at 1350° C. and showed the dielectric constant 95.8, dielectric loss 1.2×10^{-4}, and no water absorption.

Similar materials, particularly for electrical condensers, are made by sintering compositions consisting primarily of titanium dioxide with small amounts of oxide of cadmium, bismuth, zirconium, thorium, and zinc,[53] or by strongly igniting lead titanate[54] or zinc titanate.[55] Kuwa and Ito[56] shaped and fired a mass containing 80 parts titanium dioxide, 10 parts zirconium oxide, 8 parts clay, and 2 parts rare earth carbonates.

A barium titanate ceramic product, having low loss factor and comparatively high dielectric constant and stable over a wide temperature range, was produced by calcining at 900° to 1100° C. a mixture of barium oxide with hydrous titanic oxide of such proportions that the final product had a ratio of BaO to TiO_2 of 1 to 1.5.[57] The titanate was leached with acetic acid, neutralized, and dried for use as dielectric. An improved product was produced by firing mixtures of barium titanate and strontium titanate for 4 hours at 2250° F.[58] This crude ceramic material was ground, pressed into disks, and fired at 2400° C. The dielectric properties of barium titanate have been studied in detail by a number of workers.[59] The dielectric constant is independent of frequency; a sharp maximum in dielectric properties is exhibited at the Curie temperature; polarization in an electric field is fairly constant up to a temperature of 110° C. and then drops off. Application of a strong direct-current field increased temporarily the permittivity and dielectric loss.

To develop specific properties, a ceramic insulator consisting primarily of titania was heated under oxidizing conditions to render it nonporous and free from lower oxides, and then cooled from a temperature of 1000° C. at such a rate as to give the desired electric loss factor.[60] Compounds such as barium peroxide or antimony pentoxide, which liberate oxygen, could be added to the original mixture before calcination to accomplish the same results.[61] According to Haglund,[62] the silica content of an insulating composition containing 20 to 50 per cent of this component and 50 to 80 per cent alumina could be replaced wholly or in part by titanium dioxide.

Shaped insulating materials are obtained by mixing titanium dioxide with an organic binder, followed by molding, drying, and baking. As a condenser dielectric, Safford[63] employed calcined titanium dioxide of such electrical characteristics that, mixed with

10 per cent shellac and molded into a disk $\frac{1}{8}$ inch thick and 4 inches in diameter, it possessed at 1000 cycles a power factor of not more than 3, and a dielectric constant of at least 22. A mixture in tape form of finely divided titania in a solid polymerized olefin (polystyrene) has been employed as an electrical insulating material.[64] The hardened strip, prepared by applying titanium dioxide powder with cellulose acetate as a binder to a thin film of polystyrene, may be cut into sheets and assembled with sheets of foil into a capacitor with a phenolic molded casting.[65] Safford [66] employed synthetic rubber, alkyd resins, polybutene, and polystyrene as binding agents.

Inutsuka [67] prepared shaped dielectrics by firing a formed composition of titanium dioxide, minium, and an organic binder in an oxidizing atmosphere. Coursey and Brand [68] found that substituting alkaline earth metal titanates for titanium dioxide in ceramic dielectric bodies fired at high temperatures (1350° C.) raised the permittivity considerably. Wainer [69] employed fritted mixtures of titanates and stannates or zirconates in capacitors. Extremely low power factors and positive or negative temperature coefficients were obtained. For example, the dielectric constant for barium titanate, 1200 to 1300 at radio frequencies, was increased to 13,000 by incorporating stannates. Products of this type, having power factors below 0.1 per cent, may be substituted for mica capacitors, while others may be used as substitutes for paper and electrolytic condensers.

Dielectric constants of a number of titanates,[70] determined at room temperature, were barium 1150 to 3200, beryllium 70, cadmium 62, calcium 115, magnesium 17, strontium 155, and zinc 30. The high value for barium titanate was attributed to high ionic polarizability of the compound and to the high electronic polarizability of barium and oxygen ions. The dielectric constant and loss of barium titanate with temperature agreed with the Curie-Weiss law at temperatures above the Curie point, but at lower temperatures the results were more complicated, presumably because there were spontaneously polarized domains that gave rise to hysteresis and resonance.[71] When polarized by momentary application of a strong direct-current field, a resonance spectrum appeared and these resonances were attributed to a piezoelectric effect.

Very stable, high electrical resistances or grids are made by marking a glass surface with a titanium pencil. Extremely thin lines ruled on a glass surface are very permanent, and the titanium cannot be removed except by special chemical processes. Resistors of the order of 10^{11} ohms can be produced by this method.[72]

Welding Rods and Coatings

The ability of titanium and its compounds to stabilize an electric arc and to overcome the tendency to sputter and flicker has been known for many years, and practical application has been made of this property in the manufacture of fluxes and coatings for improved electric welding rods. Titanium dioxide also reduces the viscosity of the slag formed,[73] and greatly reduces the surface tension of the metal droplets on the electrodes, thus yielding small droplets which give more satisfactory welds.[74] Metallic arc fluxes [75] may be classified as arc stabilizers, e.g., titanium dioxide and carbonates; slag shields, including mixtures of iron oxides and silica, titanium dioxide and ferromanganese alloys, and calcium fluoride; and gas shield, in which organic material of the cellulose class is mixed with the foregoing fluxes.

In general, rutile or other natural minerals, such as calcium titanium silicate and calcium titanate, are employed as a source of the oxide because of low cost, but there are some applications which demand an arc stabilizer of a fineness attainable only by the use of the chemically precipitated oxide. Of the impurities normally present in rutile, only phosphorus and sulfur are likely to give trouble, and their proportions are well within the limits of most specifications. Actual measurements have shown that 1 per cent of the sulfur and 6 per cent of the phosphorus contained in the original composition are lost in the arcing process. Calcium titanium silicate furnishes a still more economical source of titanium dioxide, and preliminary tests indicate that it will give a quieter arc and a more brittle and easily fusible slag, although rutile remains the principal raw material for this purpose.[76]

In many phases of structural work, welding is rapidly supplementing or superseding the older method of riveting, largely because of the development of the heavily coated rod. With the increased volume of production, many manufacturers discontinued the dip method of coating and installed extruding machines which required raw materials of special properties. A common difficulty experienced in extruding is the tendency of the composition to increase in viscosity on standing, and this may disturb the uniformity of the rods or may proceed to the point where extrusion becomes practically impossible. This action has been attributed to an intermolecular rearrangement of the silicate binder, since some of the ingredients of the mix react with the sodium silicate to form gels or other big molecules. Careful tests demonstrated that the efficiency of

the titaniferous material (rutile) as an arc stabilizer increased with decrease in the particle size, but there is a limit to the size of particles that may be handled efficiently by the extruding machine, and trouble is encountered with material much finer than 325 mesh. As a rule, rutile for this purpose is ground to the point that 90 per cent will pass a 325-mesh screen.[77] In addition to stabilizing the arc, titanium dioxide acts as a fluxing agent, and having a low specific gravity it floats to the top of the weld to form a protective coating of the area.[78]
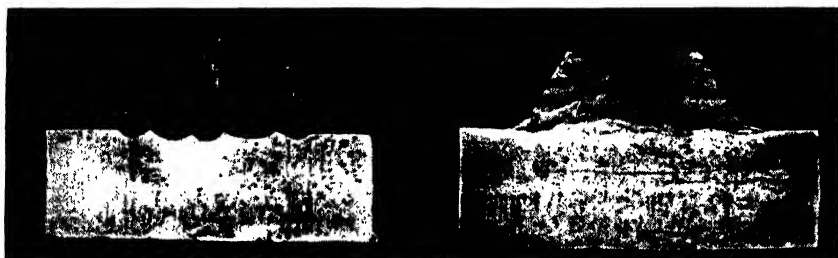
Figure 13.   Weld metal deposited from a bare iron rod and from a rod coated with a titanium dioxide composition

(Courtesy Foote Mineral Company)

Many compositions have been recommended as flux coatings of metallic rods for welding electrodes, and a few of these are given below as representative of the group. Typical mixtures contained 30 parts titanium dioxide, 20 parts ilmenite, 20 parts clay, 10 parts ferromanganese, and 20 parts asbestos powder;[79] 17 to 78 per cent titanium dioxide, 15 to 53 per cent silica, and a total of 8 to 33 per cent aluminum oxide; 4 parts titanium dioxide, 4 parts ferric oxide, 2 parts sodium carbonate, 1 part silica, and 0.5 to 5 per cent calcium hydroxide;[80] titanium dioxide 10 to 25, magnesia 1 to 8, silica 30 to 40, ferrous oxide and manganous oxide 25 to 40, and sodium oxide 2 to 6 per cent; rutile 21, quartz 26.5, kaolin 10.5, a mixture of iron and manganese ores 27.5, and ferromanganese 14.5 per cent, together with a binding agent.[81] Still another flux consisted of 54 to 60 per cent rutile and ilmenite, together with plastic clay as a binder;[82] and a similar product consisted of an equal mixture of titanium dioxide and diaspore.[83] Lair[84] coated electrodes with a flux produced by incorporating a cellulosic material with a mixture of 8 parts low carbon ferromanganese and 100 parts each of feldspar, titanium dioxide, and aqueous sodium silicate.[85] A similar composition contained 30 to 50 per cent silica, 15 to 30 per

cent ferric oxide and titanium dioxide, together with a metallic deoxidizing agent.[86] From the point of view of arc stability and appearance of the weld, a coating consisting of potassium dichromate 7.7, kaolin 30.8, pyrolusite 23.1, titanium dioxide 7.7, nickel carbonate 15.4, and chalk 15.4 per cent was recommended for use with reversible polarity.[87]

According to Tewes,[88] titanium is more suitable for effecting the deoxidation of the weld than silicon or manganese, which were formerly used for this purpose. It combines energetically with oxygen and the resulting titanium dioxide floats to the surface and can be removed with the slag. The greater homogeneity of the weld results in increased strength. Fluxes of this type for coating welding wire electrodes contain ferrotitanium alloys.[89] Typical compositions contain ferrotitanium 25, cryolite 40 to 60, and powdered asbestos 15 to 35 per cent; ferrotitanium 8 to 10, ferromanganese 16 to 24, ilmenite 27 to 39, manganese dioxide 13 to 19, feldspar 11 to 20, and kaolin up to 6 per cent; another was composed of graphite, a manganese-nickel alloy, and ferrotitanium as deoxidizing agent.[90]

Employing electrodes of titanium-bearing steel, coated with a flux consisting of 70 parts fluorite and 30 parts hydrated lime, V-butt joints of mild steel plates were successfully welded.[91] Increase in the percentage of titanium prevented blowholes in the deposited metals, but at the same time nonmetallic inclusions were increased. A similar product made by Leitner[92] consisted of a jacket of steel, containing 0.1 to 2.5 per cent titanium, surrounding a core of alkaline earth metal compound or granulated metal.

Electrodes for the arc welding of nickel and its alloys consisted of rods of the same metal heavily coated with a composition formed of 12 parts titanium dioxide, 13 parts wood flour, and 6 parts ferromanganese, with an admixture of sodium silicate to protect the wood from premature decomposition and to enter into the slag.[93] Titanium up to 3 per cent has been employed in a welding and brazing alloy for use in welding brass.[94] A representative composition contained 24 to 42 per cent copper, 0.25 to 20 per cent nickel and cobalt, 38 to 76 per cent zinc, and 3 per cent titanium. Carbon electrodes containing titanium carbide were used for welding alloys containing chromium,[95] and a flux prepared from 3 parts titanium dioxide, 48 parts marble, 8 parts ferromanganese, 3 parts ferrochrome, and 8 parts sodium silicate proved effective in welding chrome-nickel stainless steel.[96] A coating mixture for use on chromium steel wire cores used for welding chemical apparatus was composed of titanium dioxide 20 to 40, clay 15 to 20, calcium oxide 10 to 30, calcium

fluoride 5 to 15, silicon or manganese 4 to 8 parts, and sodium silicate to bind the materials together; [97] another consisted of marble 37, dolomite 10, fluorspar 32, sodium hydroxide 4.5, ferromanganese 5.5, ferrosilicon 2, ferrotitanium 5.5, starch 3.5, and waterglass 24 per cent.[98]

An eutectic alloy of 13.2 per cent titanium and 86.8 per cent iron has been used as a solder.[99]   In repairing railroad frogs by welding, low-carbon electrodes were used and the necessary hardness was obtained by alloying the weld metal with chromium, manganese, or molybdenum by additions to the electrode coatings, which also contained calcium carbonate 40, fluorspar 14, titanium dioxide 3, ferrochrome 11, ferromanganese 24, and waterglass 8 per cent.[100] Strong welds of chromium steels with high chemical resistance were made by using electrodes of similar composition and a paste of marble 25, calcium fluoride 30, ferrotitanium 20, and aluminum dust 10 parts.[101]   A heat-hardened alloy, suitable for welding electrode tips, contained copper together with 0.6 to 1.5 per cent titanium and 0.1 to 0.6 per cent each of chromium and silicon.[102] Electrodes of 18-8 stainless steel were coated with a composition consisting of titanium dioxide 20 per cent or more, silica 10 to 30 per cent, alumina up to 5 per cent, an alkaline earth metal oxide 15 to 30 per cent, carbon dioxide 7 per cent or more, and fluorine 2.5 to 10.0 per cent.[103]   During World War II the Germans made extensive use of ferrotitanium in welding rod manufacture.[104]

A viscous saline solution for coating welding electrodes by immersion is prepared by the reaction of potassium bifluoride with titanium tetrachloride.[105]   The liberated hydrochloric acid is neutralized with a base, and alkali metal chlorides are added to the composition.   For welding special alloys, these compositions may also contain salts of some of the special metals of the alloy.

Chapter 25

CERAMICS

Porcelain

In the porcelain industry, titanium has long been used to give a beautiful honey-yellow color under the glaze. During the firing operation the glaze and pigment fuse together to produce a softness of coloring and depth and richness of tone that cannot be obtained in muffle colors. The underglaze effect is a part of the ware itself, and not a coating that can crack or peel off. Colors that can be produced in this manner are extremely limited, for the high temperatures maintained in firing the ware destroy all but the most refractory materials. In addition to titanic oxide, uranium and iron compounds applied under the glaze produce a yellow color, but uranium compounds are too expensive for ordinary use, while iron oxide is somewhat erratic in the tone or shade produced. For this purpose, better grades of the mineral rutile are usually employed, and the rich yellow color may be varied by mixing in other metallic oxides. In firing, a neutral or oxidizing atmosphere must be maintained, otherwise the titanic compound may be reduced to the trivalent state, which has a bluish color.

Relatively pure grades of titanium dioxide are used to impart a natural yellowish cast to artificial teeth. The intensity of the coloration depends upon the proportion of the oxide added, and to cover the natural range from 0.5 to 5 per cent is required.

Enamels

The expectation that titanium dioxide would be widely used for opacifying ceramic enamels has not been realized. It gives a yellowish color in the presence of traces of iron, which is always present in the components, and its opacifying power is not very great, so that proportions of at least 10 per cent must be employed. Such high amounts always produce a yellowish tint, which is generally undesirable.[1] Attempts have been made to counteract this effect by adding lime and blending in other opacifiers, and the most effective of

these agents are antimony compounds.[2] Such a mixture, to be added to the frit, contained lime 14 to 25, calcium fluoride 5 to 24, antimony trioxide 35 to 43, and titanium dioxide 25 to 32 per cent.[3] A similar composition contained barium oxide as the base-forming constituent, and an oxidizing agent, such as nitric acid.[4] A preformed product, having the general formula $Sb_2O_3 \cdot TiO_2 \cdot 2CaF_2 \cdot 2 \cdot 5CaO$, has been recommended as an opacifier.[5] A low-melting (1200° F.) lead borosilicate glaze for decorating glassware consisted of lead oxide 50 to 70, silica 12 to 25, boric anhydride 1 to 10, and titanium dioxide 1 to 8 per cent.[6] The latter component was incorporated by fusing with the other ingredients of the glaze. A similar composition, with a slightly higher melting point, contained a fluoride of an alkali metal or ammonia. As an acid oxide in sheet enamels, titanium dioxide proved especially well suited as a substitute for borax and boric acid.[7] Employing white glazes and enamels from titanium dioxide, the enameling [8] was greatly improved if the alumina content was kept above 12 per cent.

In a simple enamel glass, titanium dioxide increased the fluidity; [9] for example, at 1520° F., such products were more fluid than those with like additions of alumina, zinc oxide, silica, stannic oxide, and antimony pentoxide. The color produced by titanic oxide depended upon the composition of the mix, and in the presence of antimony enamels with 14 per cent or more of this agent gave good results. It is a powerful flux and dissolves too readily to be a good mill-addition opacifier. Although the desired opacity may be produced by titania alone, the resulting enamel is colored, but this characteristic does not exclude its use in colored or ground enamels for steel sheets and cast iron.[10] In enamels containing boron, the solubility of the titania can be decreased by incorporating aluminum oxide, but the viscosity increases to such an extent that it is better to prepare a frit.[11] According to Bollenbach,[12] titanium dioxide may be substituted for fluorides, oxides of boron and tin, and other agents used to impart turbidity. Difficulties regarding fusibility and expansion of vitreous enamels may be avoided by replacing 6 to 10 per cent of the silica by titania.[13] Ceramic coatings of conventional ground-coat frits, with additions of titanium dioxide, exhibited high resistance to chipping under repeated thermal shock and to oxidation for long periods at temperatures up to 1250° F.[14]

The addition of titanium dioxide increased the chemical resistance of enamels without increasing their fusion point.[15] Specific resistance to temperature of titanium-containing porcelain was found to be inferior to that of good steatite bodies.[16] The effect of alkali

metals was comparatively slight, but the mole ratio of titania to alumina had considerable effect; high alumina products showed good resistance, and decreasing alumina and silica and increasing titanium dioxide reduced the resistance. Sintered rutile bodies had no superior.

A study of titanium-bearing porcelain enamels showed that rutile particles recrystallized as needles, while anatase appeared as irregular, rounded particles.[17] With increase in firing temperature or time of firing, the amount of anatase decreased and that of rutile increased, and at the same time the color changed from a bluish white to a yellowish white. The change in color seemed to be related to the scattering of blue light by smaller particles present at lower temperatures. Although clay used in the mill addition for titania-opacified enamels was an important factor, chemical composition and physical state had no predictable effect upon the properties of the enamel.[18]

Addition of titania up to 2 per cent increased the resistance to crazing of a typical glaze for semivitreous dinnerware, but larger proportions showed no further improvements.[19] Seven per cent produced a semimatte, and 12 per cent a porous matte effect. In such a composition the incorporation of 2 per cent of this agent gave a faint ivory color and 7 per cent a decided yellow.[20] It hardened the glaze and eliminated pitting and pinholing. The color effect varied with the temperature employed, as well as with the form of addition. Lead titanate was beneficial over a narrow temperature range. A lead silicate frit [21] for use in making glazes was prepared by fusing a mixture of 73 parts lead monoxide, 23.5 parts silica, and 3.5 parts titanium dioxide. An equivalent amount of lead titanate was also used as the source of titanium.

In an extensive study, several series of mixtures of natural rutile and purified titanium dioxide, with clays containing various proportions of iron, were prepared and burned. With low percentages of ferric oxide, a light cream color was obtained, but as this constituent increased the color ranged through tan to a greenish gray.[22] Processed titanium dioxide had a tendency to crystallize on the clay body, while rutile gave variable color effects, due entirely to irregularities in burning. The presence of titania sometimes resulted in bluish or purplish colors [23] which most frequently developed in products burned to the sintering point or in a reducing atmosphere. Clay fragments fritted together in a furnace were colored blue by lower oxides of titanium, produced during firing from the rutile present in the raw materials.[24] Reducing conditions favored the coloration, but

it also developed in the oxidizing flame if only a small amount of air was admitted. Titanic oxide, heated in an atmosphere of hydrogen above 500° C., became light blue and then dark blue. At 1340° C. the reduced oxide was almost black, and in an atmosphere of carbon dioxide above 1300° C. pure titania assumed a dark-gray color.

Reversible photosensitivity or phototropy, exhibited by many glazes containing natural rutile or chemically precipitated titanium dioxide, was found by Williamson [25] to be a property of the crystalline materials suspended in the glaze and not to the glassy part. Artificial nonphotosensitive anatase was converted to sensitive rutile on calcination with a small proportion of glaze. The presence of a considerable proportion of iron reduced the phototropic tendency.

Vitrified Ware

For the manufacture of vitrified ceramic ware, Cannon [26] recommended fire clay, with a ceramic flux consisting of approximately 68.8 per cent silica, 15.8 per cent alumina, 0.3 per cent titanic oxide, 2.5 per cent ferric oxide, 0.1 per cent manganous oxide, 2.8 per cent lime, and 3.3 per cent magnesium oxide. A shaped, vacuum-tight ceramic body may be made by heating a mixture of 50 parts each of titanium dioxide and magnesium oxide and 12 parts of an alkaline earth metal silicate bonding agent.[27] Such a material can be fusion-sealed to glass.

Thread guides, ceramic capacitors, and other articles may be formed by using a casting slip consisting of titanium dioxide with 10 per cent of a mixture of sodium alginate and montmorillonite.[28]

Friedberg, Petersen, and Andrews studied [29] the effect of composition on properties of titanium dioxide enamels. Superopaque, acid-resistant enamels were developed. Small amounts of chromic oxide produced a cream color, but large additions of ferric oxide caused no appreciable color change; firing time and temperature are most important. Magnesium oxide increased the reflectance. Lewis [30] found that purple of Cassius, in small amounts, acts as a decolorizer for titanium enamels tinted with iron or chromium compounds.

Pigments

Ceramic bodies may be purposely colored by pigments obtained on heating a mixture of oxides of titanium, antimony, and chromium with sodium hydroxide.[31] Stillwell [32] produced a lemon-yellow pigment of the formula, $4PbO \cdot Sb_2O_3 \cdot 4TiO_2$, suitable for coloring

vitreous enamels by heating the constituent oxides together at 1070° C. A yellow to brown ceramic pigment was produced by calcining titanium dioxide with minor proportions of oxides of chromium and tungsten.[33]

Titanium may be employed as a constituent of metal mixtures, used as a substitute for gold, for use in firing enameled or glazed porcelain.[34]

Glass

Titanium dioxide has been employed as the acid component in the manufacture of glass, and it may displace the silica altogether.[35] It tends, however, to make the product semiopaque. For example, the addition of small proportions to boric oxide mixtures results in an opal-like appearance.[36] It may be added to a normal charge as coloring agent, and blue or violet shades can be obtained by employing a reducing atmosphere in the melting furnace.[37] These colors may also be produced by adding lower oxides of titanium directly to the mix rather than producing them in place. Glass of this type has a high heat-absorbing capacity. A series of melts of soda-lime-silica glass cullets, made in contact with titanium metal at 1225° C. in an atmosphere of hydrogen to prevent oxidation, showed gray and black fogs with reddish zones.[38] Beyersdorfer[39] attributed the discoloration to complexes of the $TiO_2 \cdot FeO$ system and also to reduction products of the titanium dioxide.

Titanium dioxide hinders the devitrification of glass, renders annealing easier,[40] increases durability and index of refraction,[41] and decreases the power factor at high frequency.[42] Titania produces glasses having index of refraction and other properties quite similar to those containing equal molecular proportions of lead.[43] Such additions make it easier for coloring ions to take part in the glass network.

As little as 1 per cent of this constituent increased the resistance of silica glass to acids.[44] Sheen and Turner[45] prepared a series of glasses of the composition $6SiO_2 \cdot xNa_2O \cdot yTiO_2$, where x plus y equals 2, and studied the properties of the samples. No difference was observed in working until 15 per cent or more titania was present. As the sodium oxide was replaced, the solubility in boiling water decreased, but the solubility in alkalies did not fall off until 10 per cent titanium was included in the system. Above this value, the samples were superior to those containing high percentages of silica. The annealing temperature rose rapidly with increasing proportions of titanium dioxide. As the sodium oxide was replaced, the thermal

expansion decreased considerably and the index of refraction increased. A glass containing 89 to 95 per cent titania and 5 to 11 percent silica, prepared from vapors of titanium tetrachloride and silicon tetrachloride, had a temperature expansion less than that of silicon dioxide.[46] Sun[47] produced a chemically durable optical fluophosphate glass of both crown and flint types with high blue dispersion ratios. A typical composition was $NaF-TiO_2-Al(PO_3)_3$.

Colorless glass containing titanic oxide is opaque to ultraviolet light. However, by treating the raw materials with sulfuric acid to dissolve the iron and titanium compounds the product will transmit these radiations.[48] In soda-lime-silica compositions containing cobalt, replacement of the acid constituent by titanium dioxide increased the hardness and acid resistance, while the resistance to alkalies was lessened.[49] At the same time the expansion coefficient increased. Titania-alumina-silica glass possessed a thermal expansion somewhat greater than 20×10^{-7} per degree Centigrade.[50] A characteristic fluorescence in ultraviolet light was detected in some glasses containing titania.[51]

An optical glass of high refractive index contained less than 25 per cent silica and more than 20 per cent titanium dioxide.[52] The stems and bases of vacuum tubes have been formed of a glass portion fusion-welded to another section composed primarily of oxides of titanium and magnesia.[53] A material suitable for sealing to glass, in the manufacture of the envelopes of electrical discharge devices and electric lamps, consisted of a mixture of 20 to 35 per cent beryllium oxide, 80 to 65 per cent magnesium oxide, and 0.2 to 2 per cent titanium dioxide.[54] Long[55] added titania and a reducing metal, such as aluminum, to a soda-calcic glass mix, fused the batch and held it close to the softening temperature to effect swelling and formation of a sponge-like or multicellular structure.

Refractories

Ceramic bodies consisting essentially of titania have been employed as refractories, although appreciable proportions of this component in fire clays is objectionable, as it tends to lower the melting point of the product.[56] According to Duguid,[57] the chemical composition of an ideal refractory for use in furnaces up to 2700° F. corresponds to silica 54, alumina 38, ferric oxide 1.5, titania 2.2, and alkali and alkaline earth oxides 0.7 per cent. Kato[58] briquetted and sintered several types of magnetic sands and found that the sintering temperature increased with the titanium dioxide content. For

example, a sand free from this constituent sintered at 1100° C., while another, containing 15.2 per cent, was only slightly affected at 1250° C. The addition of 1 to 2 per cent to the stock toughened silica brick and reduced the spalling tendency.[59]

Shaped articles were produced by heating pulverent titanium dioxide in a mold, under pressure, at a temperature below the melting point, and cooling.[60] Alternatively, the titania was heated above the softening point and cooled quickly. Refractory crucibles have been made by firing titanic oxide at 1400° C.[61] On treatment with hydrochloric acid, uncalcined titanium oxide formed a plastic mass of the second order which was readily shaped into the desired form. Products suitable for spark-plug insulators were made by firing an intimate mixture of nonplastic titania and a binder.[62] Refractory and chemically-resistant ceramic articles were prepared by calcining shaped articles of rutile or processed titanium dioxide in a reducing or neutral atmosphere at 800° to 1000° C. until they assumed a black color.[63] Such products were good conductors of heat and electricity. A nonporous refractory material, suitable for lining glass tank furnaces, was prepared from a melt containing at least 75 per cent alumina and less than 5 per cent alkali oxide, by incorporating in the mass, alternately, small portions of carbon and rutile.[64] The addition of 4 per cent titania to magnesite improved the porosity at lower burning temperatures, around 1200° C.[65]

Refractories, consisting primarily of titanic acid prepared by the ordinary ceramic methods, may be rendered electrically conductive by heating under nonoxidizing conditions.[66] As an example, a mixture of 90 per cent titanium dioxide, 8 per cent soapstone, and 2 per cent clay was formed into the desired shape, fired as in making porcelain, heated in an atmosphere of coal gas at 1000° C. for 5 minutes to form lower oxides, and cooled in the same gas.

Titanium compounds have also been used for bonding agents in conventional refractories.[67] Such an aggregate was mixed with 5 to 15 per cent of a halide of titanium, sufficient phosphoric acid was added to convert the compound to phosphate, and the mixture was calcined according to customary procedure.

On burning, titanium dioxide in silica brick changes mostly to a glassy phase of a characteristic yellowish color.[68] Two per cent of this constituent lowered the refractoriness only about 0.5 cone, and with a simultaneous addition of 0.5 to 1.5 per cent alumina or ferric oxide, from 1 to 2 cones. The deformation temperature was not affected by proportions under 3 per cent. The addition of economically feasible amounts of titanium dioxide to high temperature

magnesium oxide refractory did not lower the coefficient of expansion significantly.[69]

Artificial Stones

Titanium dioxide has been used to produce white finishes in artificial marble. In preparing artificial stones by fusion of refuse clinker, the composition may be controlled by adding a titanium dioxide fluxing agent so that the mass does not solidify in a vitreous condition.[70]

Grandlach [71] developed a method of coloring granules of quartz, slate, and traprock for use in composition roofing, by which the desired pigments were attached to the surface by a waterproof cement consisting of the reaction product of phosphoric acid and titanium dioxide. The mass was heated to 200° to 425° C., with agitation, to prevent agglomeration.

In preparing shaped articles, Nagai [72] mixed pulverized titanium dioxide with a suitable amount of an oxidizable metallic powder (zinc, iron, aluminum, lead, or magnesium), and to this base added, first, a small proportion of a metallizing agent such as zinc chloride, ferric chloride, ammonium chloride, or cryolite, and then a minor proportion of zinc, ammonium, or aluminum nitrate, and finally a small amount of aluminum or zinc hydroxide to give plasticity. The mass was molded dry, or with a very small proportion of water, under pressure, and heated at a high temperature to effect solidification.

Chapter 26

MORDANTS AND DYES

Textiles

As early as 1885, Barnes recognized that titanium compounds could be used in mordanting yarns, and in 1896 Proctor suggested their use in dyeing leather. Later, the problem of obtaining a compound suitable for this purpose from the titaniferous residues of alum works was attacked, and a salt of the composition $TiO(SO_4Na)_2 \cdot 2H_2O$ was prepared which was sufficiently free of iron to be used in mordanting wool. This material was placed on the market, and later the double oxalate of titanium and potassium, especially suited for dyeing leather, made its appearance. In 1901 Knecht proposed titanous salts as stripping agents. The tetravalent salts have been used for fixing tannin on cotton.[1] By employing solutions of titanic chloride, to which a small proportion of sodium acetate had been added, Barnes[2] obtained pleasing colors on cloth with alizarin and other dyestuffs, and since this beginning, other compounds, such as the sulfate, fluoride, lactate, tannates, tartrates, and double salts with the alkali metals (particularly oxalates) have been used for the fixation of colors on textiles.

In addition to serving as good mordants for basic dyestuffs, titanium tannate in oxalic acid solution acts as a dye in its own right and produces yellow and golden shades on textiles, particularly on mercerized cotton. In tartaric acid solution, the salts are used in calico printing.

As a mordant with some dyes, titanic oxide is reported to be much superior to alumina. From alizarin yellow a mordant is obtained as brilliant as that produced with alumina, and alizarin scarlet, dyed on a titanium mordant, is one of the fastest colors wool can take.[3] The titanium dioxide for this purpose must, however, be free from iron. In staining, dyeing, or mordanting textiles and leather that have been previously treated with tannic acid with a solution of a mixture of titanium and iron salts, shades from the yellow of titanium alone to gray or black, produced by iron alone, may be

467

obtained by adding sodium carbonate or sulfuric acid to vary the hydrogen ion concentration.[4]

Fantasy effects can be produced on cotton or linen fabrics having transparent parts by impregnating the material with aqueous titanium chloride and adding sodium hydroxide to form an insoluble hydroxide or oxide.[5] The precipitate adheres firmly to nontransparent areas, leaving the transparent regions in an unchanged condition.

In printing cloth, the hydrous oxide of titanium was worked into a paste with an equal weight of water, passed through a 250-mesh screen, and applied to the fabric with albumin, viscose, or acetylcellulose in acetic acid solution.[6] The covering power was slightly greater than that of an equal weight of zinc oxide, and four times that of barium sulfate.

Titanium salts of azomethine compounds may be used to produce orange and red lakes,[7] and similar products with acid polyazo dyes may be employed in dyeing wool and leather brown shades.[8]

Perhaps the largest use of titanium compounds in the dye industry is for stripping dyestuff from cotton, wool, and silk,[9] and for this purpose a trivalent salt, usually the sulfate or chloride, is employed. Hot dilute solutions of these compounds are useful in reclaiming goods that have been dyed unevenly or a wrong shade. Azo dyes on cotton fabrics are rapidly destroyed, especially by the chlorides. After the stripping operation, which normally requires less than a minute, the material may be washed and redyed immediately. The amount of titanium chloride, for instance, required for this operation depends upon the color and character of the dyestuff and varies from 1 to 10 per cent of the weight of the textile treated. The salt destroys basic dyestuffs that have been formed with tannin-tartar emetic mordant, although the fiber assumes a brownish color, because of the formation of titanium tannate. It is also employed to discharge "ingrain color dyed" cotton.

Organic acids, such as citric, tartaric, oxalic, and succinic, and their alkali metal salts, may be added to sulfate or chloride solutions of trivalent titanium for stripping and discharging dyes.[10] The organic radical may be partially substituted for the inorganic, with the result that the solution becomes more stable and may be safely concentrated to the point where it becomes solid or semisolid on cooling.

Knecht [11] employed titanous thiocyanate for discharging or stripping dyed yarns and fabrics and in producing various discharge effects.

Titanous salts have also been employed as a bleaching agent for cotton, silk, and wool, and dilute solutions have been used to clear up the white portions of fancy colored goods.

Leather

Titanium compounds have gained considerable application in the leather industry. An important salt is the double titanium and potassium oxalate, which serves the dual role of acting as a mordant and of precipitating any residual tannin from vegetable-tanned leather that might throw down dyestuffs in this operation, particularly if basic agents are employed. Used as a striker with logwood to produce black, salts of titanium do not cause the leather to become brittle, as do equivalent compounds of iron. Potassium titanium oxalate serves as an excellent direct dye for tanned leathers and produces a yellowish-brown color stable to light, alkalies, and wear. It is especially suitable for shoe leather. The tan shade may be modified by varying the tannin material and by the addition of other dyes; such compounds may be used with either vegetable- or chrome-tanned leather to produce a great variety of fast colors by employing the proper dyes. For example, on chrome-tanned leather with sumac extract, it produces a lemon yellow; with logwood, a violet and a black; and with Lima extract, a magenta. The double lactates and tartrates may also be used. Potassium titanium oxalate not only fixes tannin on the leather, but because of its yellowish-brown color lake, much less dyestuff is required.[12] With tannides, titanium salts produce a light brownish-yellow color of great strength and uniformity, and are suitable for dyeing furs and high-grade leathers.[13] The amount of synthetic dyes required, however, is not lowered by the presence of these compounds. Greater uniformity of color of chrome-tanned calfskins, processed with acid dyes, is obtained with the use of titanium salts.

Compounds readily soluble in water and suitable for tanning and weighting agents were obtained by adding sodium carbonate to a solution of titanium sulfate, in such proportions that 0.3 to 0.5 mole sulfuric acid was combined with each mole of titanium.[14] Spence and Crundall[15] prepared soluble hydrolyzable compounds that are soluble only with difficulty, for use in tanning and mordanting, by evaporating a solution of titanium phosphate in oxalic acid or sodium hydrogen oxalate.

For producing leather from calfskins, the hides were impregnated with a solution containing lactic acid and a Werner complex of tita-

nium sulfate, with an organic acid or a salt thereof, and an insoluble titanium oxide was precipitated in situ in the hide by adding sodium carbonate and water at intervals.[16] According to a related process, pickled calfskins were subjected to the action, first, of an acidic polymeric carboxylic material, and then to the action of a soluble salt of titanium or other metals.[17]

Skins to be finished in light shades are normally treated with white pigments to overcome the greenish-blue color derived from chrome tanning agents, and titanium dioxide, because of its high opacity and resistance to residual chemicals such as sulfides and acids, is especially well suited for this purpose. Because of the small amount of the pigment required, usually 1 or 2 per cent, based on the wet leather, the flexibility of the skins will not be materially changed. The pigment may be added during or after the drumming operation, in which the skins are treated with an emulsion consisting of cod-liver oil, neat's-foot oil, sulfonated oils, and water to lubricate the fibers and give the leather the desired softness and pliability and to increase its tensile strength and resistance to tearing. Both methods of addition give very satisfactory results.

Leather that has been whitened, drummed, and dried rarely meets the demand of the consumer without further treatment, so tannery finishes are applied. Titanium dioxide is well suited for white and tinted coatings. The pigment is usually ground in sulfonated castor oil or glycerin, the paste is thinned with casein solution to the proper consistency for application, and formaldehyde is frequently incorporated to increase the water resistance. Although these compositions vary considerably, in general they contain mixtures of casein, albumin, gum tragacanth, shellac, and waxes, in addition to the pigment. Titanium dioxide is generally preferred for finishing grained leather, so that opacity may be obtained with thin coats without obscuring the effect or filling the pores. Shoe manufacturers use heavier compositions of this type to cover up scuffings and blemishes which almost invariably occur during processing.

White shoe dressings of both the paste and liquid types employ titanium dioxide as the pigmenting agent, but for this purpose the water-dispersing grade should be used.

Metallized Dyes

According to Hauser and Levite,[18] two hydroxyl groups in the ortho position to one another are necessary for the formation of colored, stable complexes with titanium which fall in with Lieber-

mann's definition of mordant dyes and color lakes. Such compounds do not give the reactions characteristic of titanium ions. Complex metal dyes for use with silk, wool, or tanned leather may be prepared by treating diazo dyes, obtained by coupling two different compounds of this class, with a compound of titanium.[19]

Compounds of azo dyes, in which molecules of the same or different dyes are attached to the metal, can be prepared by treating a titanium compound of one of the dyes with the same or a different azo dye capable of fixing the metal.[20] Dyes obtained from 1-diazo-2-hydroxy naphthalene-4, 6-disulfonic acid, and a coupling component, such as beta-naphthol, were treated with a titanium salt to obtain a metalliferous product which gave fast colors on dyeing.[21] Similar products were prepared by treating o-hydroxyazo dyes with the product obtained by reaction, in the presence of caustic alkali, between a polyhydric alcohol, such as glycerin, and titanium hydroxide.[22] Such dyes gave fast colors. Pigment dyes containing a heavy metal azomethine diarylene dihydroxylates were prepared by the action of ortho hydroxybenzaldehyde and ortho aminophenol and various related compounds with salts of titanium.[23] Similar complex compounds, obtained by treating azo dyes with salts of titanium, were used as dyes for lacquers.[24] The compound, $Ph_2 \cdot TiCl$, reacted with nitric oxide to give an 8 per cent yield of the diazo compound, $PhN_2 \cdot NO_3$.[25] Dyes readily soluble in organic solvents were obtained by the reaction of titanium compounds with azomethine.[26] The reaction of aminobenzenearsenic acid with 2-furaldehyde, under controlled conditions, was reported to give Stenhouse dye which formed colored salts with titanium.[27] Complex metal compounds, suitable for dyeing artificial resins or nitrocellulose lacquers, were obtained by heating in an aqueous medium basic dyes, such as brilliant glacier blue, with titanium-containing dyes free from sulfo and carboxyl groups of the anthroquinone, triarylmethane, logwood, or catechu types.[28] Such products showed good color fastness. A solid compound, formed by the reaction of titanium tetrachloride with glycerol, in aqueous solution, was an excellent precipitant for all sulfonated dyes.[29] It gave strong, soft-textured lakes with aluminum hydroxide, and hard lakes if used alone. The compound precipitated many dyes not affected by barium chloride.

Chapter 27

CATALYSIS

Titanium and its compounds, particularly the dioxide and tetrachloride, have been found to catalyze many organic and inorganic chemical reactions and rearrangements.[1] These agents are adapted to a wide variety of conditions, since the oxide is a relatively insoluble refractory solid and the chloride is a relatively volatile liquid, soluble in both organic and inorganic media.

Inorganic Reactions

Titanium dioxide functions as a catalyst in the decomposition of nitrous oxide [2] and in the reaction between carbonyl sulfide and sulfur dioxide.[3] Mixtures with ferric oxide, nickelous oxide, and cuprous oxide showed greater activity toward oxidation in air at 150° C. of a 12 per cent mixture of carbon monoxide.[4] The photochemical oxidation of an air-containing aqueous solution of ammonia was strongly accelerated by titanium dioxide in the ultraviolet of wave length 3000 Ångstrom units, and was also sensitized by violet, blue, and green light.[5] Since neither titanium dioxide nor ammonia absorbs in this spectral region, the surface layer was thought to be the seat of the absorption and of the subsequent reaction.

A mixture of oxides of titanium, tantalum, and columbium showed definite catalytic properties in the oxidation of sulfur dioxide in the contact sulfuric acid process.[6] Apparently the two oxides activated the titania. The composition was very stable, and, if poisoned, it could be completely regenerated by igniting in air at 500° to 550° C.[7] This oxide alone, however, has been reported to be less effective than iron oxide. The reaction mechanism has been proposed by Neumann.[8] An initial quantity of basic titanium sulfate ($TiOSO_4$) formed and further reacted as follows:

$$4TiOSO_4 + 2SO_2 \rightarrow 2Ti_2(SO_4)_3$$
$$2Ti_2(SO_4)_3 + O_2 \rightarrow 4TiOSO_4 + 2SO_3$$
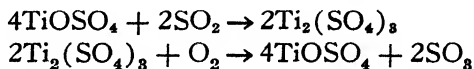
An active catalyst was prepared by applying a solution of titanium tetrachloride with platinum or palladium to a porous inert support,

such as pumice stone, asbestos, or coke, and heating the product in an atmosphere of hydrogen or carbon monoxide until the metals were deposited in an intimate mixture.[9] Alternatively, the metals were deposited on the supporting material by electrolysis.

Organic Reactions

The activity of titania as a catalyst in organic reactions was found to depend to a large extent on the method of preparation.[10] Quantitative studies were made by passing the vapors of ethyl alcohol over various samples at 350° C. and noting the volume and composition of the gaseous decomposition products. The dioxide ignited at low temperatures gave best results as a dehydration catalyst, and with increasing temperatures of processing the effectiveness decreased. Products obtained by hydroxide or hydrolytic precipitation from sulfate and chloride solutions were most efficient, while those prepared from oxalates were of least value. Other factors being equal, the activity increased with the degree of subdivision. Samples prepared from sulfate solutions remained very active after 10 hours of service. Caglioti[11] found that the dehydration-dehydrogenation ratio of ethyl alcohol was the same with the rutile or anatase crystal form as the catalyst.

Elemental titanium catalyzed the decomposition of phenylhydrazine at 150° to 170° C., but was less effective than anhydrous chlorides of nickel, zinc, and calcium.[12] It has also been employed as a catalyst in sulfonation of anthracene.[13] The maximum yield of anilin from nitrobenzene was obtained at 282° C. with a catalyst prepared by reducing nonignited titanium dioxide.[14] A precipitate, obtained by adding ammonium hydroxide to boiling dilute aqueous titanium tetrachloride, was reduced with hydrogen at 302° C.

The synthesis of hydrocarbons and their oxygen derivatives from carbon monoxide and hydrogen has been accomplished in the presence of a catalyst containing titania as one component.[15] Aromatic hydrocarbons and monovinylacetylene may be produced simultaneously by passing acetylene at 300° to 800° C. over titanic oxide.[16] A catalyst for methyl alcohol synthesis contained oxides of titanium, along with more easily reducible oxides such as those of copper, iron, cobalt, nickel, and silver.[17] Small proportions of this agent improved the activity of a catalyst consisting primarily of a sintered metal of the iron group and an alkaline earth metal halide or phosphate used in synthesizing hydrocarbons and their oxygen derivatives from carbon monoxide and hydrogen.[18]

Vapor-phase esterification of benzoic acid with ethyl alcohol gave a maximum conversion of 87 per cent at 370° to 450° C., with titanium dioxide as catalyst.[19] Maihle[20] found that the agent catalyzed the vapor-phase esterification of alcohols from methyl to isopropyl, with acids from formic to pelargonic. In a particular esterification, an equimolecular mixture of isobutyric acid and ethyl alcohol was 71 per cent reacted by passing over the titania at 280° C. With 2 moles ethyl alcohol to 1 mole of the acid, and with 4 moles of alcohol to 1 mole of acid, the yields were 83.5 and 91 per cent, respectively, based on the acid content. Above 400° C. it catalyzed the decomposition of esters of secondary alcohols and monobasic acids.[21] The products were, in turn, acids into ketones and alcohols into ethylene hydrocarbons.

A titania promoter with copper-alumina catalyst favored ethyl acetate formation by dehydration of ethyl alcohol.[22] Titanium dioxide catalyzed the conversion of carboxylic acids to aldehydes.[23] Porous copper, activated by metallic titanium, catalyzed the formation of esters by dehydrogenation of primary alcohols in the vapor phase.[24]

In the presence of a catalyst of titania and nickel, olefin polymers were hydrogenated at 170° to 350° C.[25] The nondestructive dehydrogenation of aliphatic hydrocarbons (butane) to corresponding products of lower hydrogen content was effected by bringing the material, at a temperature above 325° C., into contact with a vitreous gel catalyst consisting of chromium oxide, and an oxide of titanium that was difficult to reduce, in a highly hydrous condition.[26] Similar results were obtained with titanium dioxide alone as a porous support.[27] Chromic oxide, together with titanic oxide, has been employed as catalyst in the two-stage dehydrogenation of paraffin hydrocarbons to produce diolefins.[28] Titania, either in granular form or on an inert support, catalyzed the vapor-phase oxidation of aromatic hydrocarbons admixed with air or oxygen,[29] the direct oxidation of xylene,[30] and accelerated the oxidation of methane, but in admixture with magnesium oxide the latter reaction did not proceed beyond the formaldehyde stage.[31]

Primary amines (toluidine) were prepared by heating the corresponding secondary amines (ditolylamine) at 440° C., in contact with oxides of titanium.[32] The activity of the catalyst could be regenerated by heating it in air at a temperature sufficiently high to cause combustion of the organic impurities.

Titanium dioxide was found to accelerate the condensation of olefine oxides with water and organic hydroxy compounds, such as

monobasic alcohols and phenols, to produce glycol derivatives.[33] For example, dimethyleneglycol monoethyl ether was obtained by passing a mixture of ethylene oxide and ethyl alcohol, preheated to 80° to 100° C., over the catalyst. It also catalyzed the decomposition of ethyl acetate into acetic acid and acetylene.[34] Turwillinger [35] prepared isopulegol by agitating citronella at 130° to 140° C., in contact with titania supported on a diatomaceous earth base, which catalyzed the reaction.

Aliphatic hydrocarbons were transformed to closed chains or cyclic compounds by heating at 400° to 700° C. in the presence of oxides of titanium; [36] octane was cyclicized to orthoxylene, and the dehydrogenation of cyclohexane was effected at 400° to 550° C.[37] Titanium dioxide catalyzed the isomerization of cyclohexane into methylcyclopentene, and dehydrogenation into benzene, toluene, and xylene.[38] In the presence of oxides of titanium, chromium, molybdenum, and vanadium, such compounds as hexane, heptane, and octane have been cyclicized into benzene, toluene, and xylene.[39]

Dihydrofuran and its methyl derivatives have been prepared by bringing 2-butene-1, 4-diol, or methyl derivatives thereof, at temperatures above the boiling point of the former, into contact with titanium dioxide as a dehydration catalyst.[40] This agent has also been employed in the production of formaldehyde condensation compounds in vapor-phase reaction.[41]

A cracking catalyst for petroleum was prepared by calcining a mixture of silica and titania hydrogel.[42] Straight gasolines of low antiknock value were improved by passing them, at 400° to 750° C., over a catalyst of titania precipitated from aqueous solution and supported on a refractory base material.[43] A contact time of less than 15 seconds was sufficient. Mineral lubricating oils were freed from naphthenic acid by bringing the vaporized material, at temperatures above 300° C., into contact with a catalyst of this type.[44] Fatty oleaginous matter of vegetable or animal origin, such as palm oil and fish oil, was cracked to products similar to mineral oil by distillation at 250° to 600° C. in the presence of alkali titanates.[45] A basic oxygen, containing salt of titanium or a reduction or transformation product, was found to catalyze the hydrogenation of carbonaceous compounds.[46] Examples of such agents are titanium molybdate, chromate, tungstate, and vanadate.

The dioxide, citrate, tartrate, and lactate catalyzed the reaction between urea and formaldehyde to form resins, and tetrachloride catalyzed the polymerization of indene and cumarone.[47] Phenolic resins, suitable for use in coating compositions, have been produced

by heating dipentene with titanium chloride.[48] The titanium salt was later removed from the reaction product by washing.

Secondary and tertiary olefins, containing at least 3 carbon atoms, react with aliphatic carboxylic acids at 100° C. in the presence of titanium tetrachloride to form esters.[49] Ethers can be prepared in the same manner by substituting alcohols for acids. The tetrachloride catalyzed the reaction of benzene with ethylene in the presence of hydrochloric acid to produce derivatives containing from 1 to 6 ethyl groups,[50] and it formed a homogeneous mixture with the hydrocarbon products. Secondary and tertiary alkyl monochlorides have been prepared from normal liquid olefins, such as those from cracked benzene, by passing the vapors mixed with hydrochloric acid over titanium tetrachloride deposited on silica gel or active carbon at temperatures of 150° to 180° C. in succession.[51] In the presence of this compound, benzyl ethyl ether in benzene decomposed into benzyl chloride which entered into a secondary reaction with the solvent to form mono- and di-substituted products.[52] Preformed benzyl chloride reacted in the same manner with benzene. Similarly, ethoxydiphenyl methane (Ph_2CHO Et) reacted with benzene in the presence of titanic chloride to produce triphenyl methane, while under equivalent conditions triphenyloxydiphenyl methane (Ph_2CHO C Ph_3) gave 2,2,2-triphenylethanol (C Ph_3CH_2 OH) and no tetraphenyl methane.[53] The agent catalyzed the reaction between ethers, such as diethyl, benzyl-ethyl, and phenyl-ethyl with sulfuryl chloride,[54] and also the polymerization of cyclopentadiene.[55]

The very powerful action of titanium tetrachloride made it possible to convert tetraacetyl-beta-methylglucoside quantitatively and without decomposition into the alpha form, on a water bath, in 4 to 5 hours.[56] In chloroform it catalyzed the racemization of 2-phenylchloroethane (MePhCHCl),[57] but the rate of the change varied considerably with the concentration of the tetrachloride present. Tetraacetyl-beta-hexyl glucoside and tetraacetyl-beta-cyclohexylglucoside were converted to the alpha form by treatment with this agent.[58]

Aluminum chloride, containing a small proportion of titanium tetrachloride, catalyzed the synthesis of aldehydes (benzaldehyde) by the reaction, under pressure of carbon monoxide with an aromatic hydrocarbon (benzene) or a halogen derivative (chlorobenzene).[59] The catalytic activity of titanium tetrachloride in the Zincke, Ullmann, and Friedel and Craft reactions was reported to be greater than that of chromium but considerably less than that of cerium, thorium, or aluminum chlorides.[60]

Titanium fluoride has been used as a catalyst in the synthesis, under pressure of organic acids,[61] and in the presence of more than 5 g. of the sulfate per liter, the electrolytic reduction of ferric sulfate to the ferrous state proceeded to completion and the current efficiency was considerably increased.[62] The citrate, tartrate, and lactate have been used to catalyze the formation of phenol-formaldehyde resins.[63]

Polymerization of isobutene in hexane with titanium tetrachloride catalyst took place very slowly in a closed system at 90° C. and dry air, nitrogen or oxygen had no effect, but if laboratory air or nitrogen containing water vapor was bubbled in, a rapid reaction took place.[64] In the Friedel and Craft ketone synthesis, the maximum yield was obtained at titanium tetrachloride-acid chloride ratios several times greater than the 1 to 1 value often recommended.[65] The tetrachloride catalyzed the hydrolysis of casein, gelatin, and peptones.[66]

Titanium dioxide, calcined at a high temperature, has been employed as a support for catalysts.[67]

Connolly [68] prepared a composite titania gel-boria catalyst. Ammonium hydroxide was added to a solution of titanyl sulfate to precipitate the titanium as the jelly-like hydrous oxide, and this was washed until peptization began, dried, heated, and rewashed. The gel was then impregnated with sufficient orthoboric acid solution to add 5 to 20 per cent boric oxide, and the mixture was activated by heating at 800° F.

Chapter 28

SPECIAL APPLICATIONS

Gem Stones

White fluorescent diamonds [1] were obtained by quenching carbon containing ferrotitanium alloys in water from 1600° C. or higher, according to the method of Moissan. Vernevil [2] made synthetic sapphires by fusing a mixture of 98 per cent aluminum oxide, 1.5 per cent ferric oxide, and 0.5 per cent titanium dioxide in an oxy-hydrogen flame. Equivalent proportions of sulfates of these metals, as the starting materials, gave similar results, but the compounds were decomposed to oxides by heat before fusion was effected. Stars of synthetic star sapphires and rubies are made from a purified form of titanium dioxide. [3] The star is a milky spot the shape of the crown of a derby hat at the apex, and from it flow down to the edges of the stone six milky-white lines making a six-pointed star. Bodies of both stones are prepared by fusing powdered aluminum oxide. The blue color of the sapphires is produced by the addition of a small proportion of cobalt or iron compounds, and the red of the rubies by minor proportions of chromium compounds. These synthetic stones are as beautiful as the natural gems, the stars of which are also composed of titanium dioxide. Large boules of clear, transparent titanium dioxide of the rutile crystal modification are produced by fusing the purified powder in an electric furnace at 3330° F., employing a special automatic feeding arrangement. [4] The boule builds up on a pedestal of zirconium. Cut gems show a play of color equal to opal and the fire and brilliance of diamond, but are more brilliant under ordinary electric lamps than in daylight. Rutile is only seven tenths as hard as diamond, but has an index of refraction of 2.7, as compared with 2.41 for diamond, which means that it reflects light to a higher degree. Pure titanium dioxide gives colorless stones, but small amounts of impurities give colors of green, red, yellow, blue, and purple. This is in contrast to natural rutile, which is opaque and of a dark red to black color. The largest stable stones it has been possible to produce weigh 85 carats; larger boules seem to fracture automatically. Rosenthal [5] produced a syn-

thetic gem stone by sintering a ground mixture of 1 part titanium dioxide, 1 part copper oxide, 8 parts ferric oxide, and 8 parts cobalt oxide.

Figure 14.   Cut gem stone and boules of synthetic rutile

Smoke Screen

Titanium tetrachloride in contact with moist air reacts with the water vapor present to form the pentahydrate, $TiCl_4 \cdot 5H_2O$, which, on further reaction with the water, breaks up into titanium hydroxide and hydrochloric acid. Under conditions of high humidity, the hydrogen chloride released condenses with water to form minute droplets of hydrochloric acid solution. If suddenly dispersed by an explosive charge, a large, dense cloud is formed by the rapid hydrolysis. The density of the cloud may be further increased in moist air by the presence of ammonia, which forms ammonium chloride with the hydrochloric acid liberated. However, if the air is relatively dry, ammonia should be avoided, since a complex compound, $TiCl_4 \cdot 6NH_3$, is formed, which has little obscuring power. For this reason the tetrachloride and ammonia are usually dispersed separately. The bulk of visible particles which go to make up the smoke are of the order of 10^{-4} to 10^{-5} cm. in diameter. According to Booker and Annis,[6] a more effective screen may be obtained by employing the tetrachloride in combination with minor proportions of sulfur chloride. The addition of 0.1 to 0.2 per cent phosphorus,

dissolved in a mixture of carbon disulfide and carbon tetrachloride, improved the stability, and the solution did not clog or corrode the spray equipment.[7]

Clouds of titanium dioxide may be formed by passing a current of air over an electric arc between electrodes of elemental titanium so as to oxidize the metallic vapors formed.[8] Mixed oxides may also be dispersed in the air in the same manner by employing electrodes of more than one metal, such as titanium and silicon or titanium and iron.

Titanium tetrachloride clouds dissipate more rapidly than those produced from white phosphorus or oleum, even under conditions of high humidity, probably because of the difference in vapor pres-

Figure 15. Skywriting

sure of solutions of hydrochloric acid as compared with phosphoric and sulfuric acids. This smoke is not injurious to man under ordinary conditions and is only slightly irritating. The liquid reagent, however, is quite corrosive to both fabrics and skin. Although the smoke is considerably inferior to that produced by white phosphorus or oleum in bombs and shells, it is widely used in airplane exhaust clouds and airplane curtains because of other properties desirable for this purpose.[9]

During World War I titanium tetrachloride was used mainly for producing smoke clouds for concealing and spotting purposes. In artillery shells, where proper conditions for use with ammonia could not be realized, it was not of much use except for ranging purposes; that is, shells filled with this agent have the same projectile properties as those filled with poison gases (mustard), and since

the burst produces a cloud, the exact range can be observed. It is less volatile than silicon tetrachloride and thus more difficult to handle in spray. For this reason it was not used by the navy.[10] In peacetime the tetrachloride is extensively used for training purposes.

Skywriting, so commonly employed for advertising and other purposes in the larger cities, is done with this agent. The clouds of white smoke observed during the fireworks displays at the New York World's Fair (1939-1940) were formed by titanium tetrachloride released by the bursting of the rockets. In skywriting, by projecting the titanium tetrachloride into air simultaneously with a surrounding sheath of a nonreactive gas such as carbon dioxide, carbon tetrachloride, or dry air, clogging of exit nozzles may be prevented.[11] If the tetrachloride is sprayed into the air intermittently, as in producing disconnected letters or figures, the tendency to clog may be further reduced by projecting the inert gas simultaneously and continuously.

Paper

An improved process for bleaching southern hard pine kraft paper consists of treating the stock first with calcium hypochlorite and later with titanous sulfate.[12] Titanous sulfate has been employed in bleaching sulfite pulp and paper discolored by age.[13] Such compounds, present in aluminum sulfate prepared from bauxite containing this element, have been reported to have a beneficial whitening action on the paper treated.[14]

Deribère[15] pointed out the possible use of titanium fluoride, chloride, and oxalate for coloring tannin-impregnated cellulosic fibers.

Photography

Rath[16] made photographic plates by securing titanium dioxide to a rigid support with a binder, and also by sintering the material into thin self-supporting slabs. On exposure, these products like ordinary plates, yielded directly grayish-green images which persisted for several hours in artificial light and for a longer time in red light or in the dark. The impressions were destroyed by heating to 100° C., and the plates could then be used again. Such images were strengthened and fixed[17] by applying a solution of potassium iodide, containing starch, before exposure. Iodine, which was then liberated to a degree proportional to the intensity of the light, gave

a distinct coloration. As before, the plates could be regenerated by heating. This image-forming action is based on the property of the dioxide of liberating oxygen on exposure to light.

Titanium dioxide is employed in the sensitized emulsion layer in photographic catatype processes,[18] in the intermediate relatively reflective stratum between superimposed images of the film in color photography,[19] in the light-scattering surface in an intermediate or back layer,[20] and in light-sensitive or image-bearing layers.[21] For best results the size of the particles should not be greater than that of the light-sensitive component, for example, silver bromide. The finely divided material is used as the light-scattering layer in multicolor photographic transparencies.[22]

Water Purification

Titanic sulfate has certain advantages over both aluminum and ferric sulfates as a coagulant for water purification.[23] For instance, it removes color and yields good flocs over a wider range of hydrogen ion concentration. The hydrous oxide forms much more readily and in a bulkier condition near 0° C., and is thus particularly effective with cold water. Even at ordinary temperatures the floc is much more bulky and opaque than that obtained from alum, but it settles more slowly. On the other hand, titanium sulfate tends to hydrolyze in the feed solution and offers difficulties unless the concentration is held rather high. This disadvantage may be further reduced by adding aluminum or ferric sulfate, or, in fact, any soluble sulfate, to the treatment solution. The compound could not be fed dry, the flocs settled more slowly, and it offered no advantages for fluoride removal. The product obtained by reacting ilmenite with sulfuric acid gave much better coagulation in discolored water containing high proportions of colloidal matter and dissolved salts than did iron or aluminum sulfate.

Laundry

In removing suspended solids from laundry waste, the soap content was hydrolyzed, the solution was passed through a filter charged with titanium dioxide to remove the freed fatty acids, and these were recovered from the filter bed by treatment with steam.[24] Titanium dioxide of pigment grade has been used as a whitening agent in laundering white articles. Trivalent compounds have been used as bleaching agents in laundries and in bleaching old rags.

Sewage

Muskat [25] employed an admixture of 0.5 to 10.0 per cent titanium tetrachloride with ferric chloride as a flocculating agent in sewage or ore treatment. The tetrachloride, combined with protein material such as gelatin, glue, and albumen, proved to be an effective coagulant for sewage.[26]

Plant Growth

A number of investigators have reported that titanium compounds stimulated the growth and development of plants. According to Arnon,[27] the growth of asparagus and lettuce in culture solutions containing no microelements was increased on adding 0.01 part per million of titanium as a neutral compound. Alfalfa without nodules, cultured in Crone's solution containing sodium nitrate, showed greatly increased growth after addition of potassium titanate, and a large amount of titanium was found in the plant, particularly in the leaves and stems.[28] Experiments with *Zea mays,* employing nutrient solutions, indicated that titanium could not be substituted for iron in the formation of chlorophyl.[29] Addition of small quantities of such salts to distilled water employed in the sand cultures of orange trees proved beneficial.[30] Titanium sulfate, titanic acid, and potassium titanate were observed to have slightly beneficial effects upon the growth of nodule bacteria.[31] Such compounds enhanced the growth of roots [32] and the mycelium growth of *Aspergillus niger.*[33] Nemec and Kas [34] found that the addition of titanium salts favorably influenced plant growth. The sugar content of beets was increased by adding these compounds to the fertilizer, along with boron and manganese.[35] Such compounds had a positive effect upon the development of red clover only if added simultaneously with boron.[36] The element increased the length of the pollen tube and the percentage of germination.[37]

Gardner [38] added compounds of titanium other than nitrides, such as oxides, titanates, and slags which contained more than traces of iron, to mixed fertilizer. On the other hand Brenchley [39] reported that small proportions of such compounds, added to commercial fertilizers, failed to improve the growth of mustard on both acid and basic soils. Sodium titanate [40] exerted no influence either with or without fertilizer, and the addition of titanium compounds to media in which there was a sufficient concentration of iron depressed plant growth.[41] Stapp [42] observed that tumors of plants were definitely increased by 0.0001 to 0.001 per cent titanium sulfate.

Rossi [43] proposed the use of titanium nitrides in fertilizers as a source of nitrogen, since the compound may be prepared from atmospheric nitrogen.

Other Applications

Hydrocarbon mixtures boiling above 250° C., synthesized from carbon monoxide and hydrogen, may be purified prior to cracking by treatment with titanium tetrachloride.[44] A small proportion of beta-diketone of titanium added to motor-lubricating oil lessened the formation of hard carbon under operating conditions.[45]

The acid sulfate can be used as a desiccating agent, as for drying gases.[46]

Booth [47] found that fluorine could be absorbed and removed from phosphoric acid by titanium dioxide. A quantity of the agent greatly in excess of that required to combine chemically with the fluorine present was introduced and after the action had proceeded to completion the mixture was filtered or settled.

Titanium compounds are employed in chemical analyses, primarily as reducing agents. Hydrous titanium oxide was found to be a very effective carrier of protactinium, and this property has been applied in separating the element from its ores.[48] On hydrolyzing a slightly acid solution containing titanium sulfate, practically all the protactinium present was carried down with the precipitate, even though precipitation of the titanium was not complete. For example, Congo pitchblende was extracted with aqua regia and the solution was evaporated to dryness. The residue was taken up in dilute hydrochloric acid, and titanium tetrachloride solution was added, followed by sodium thiosulfate to precipitate titanium hydroxide. A second treatment with the tetrachloride removed the protactinium completely. The titania precipitates were combined with the residue from the aqua regia extraction, and the mixture was dissolved in hydrofluoric and sulfuric acids. Iron, bismuth, and tin were then separated, and the titanium was extracted as ammonium titanofluoride, dried, ignited, and taken up in aqua regia. By this procedure titanium dioxide was recovered quantitatively and it contained all the protactinium of the original ore.

In preparing very pure barium metal, oxygen compounds of barium and beryllium were coated upon a refractory core of titanium which reduced the compounds at the temperature employed.[49]

An emulsion of the oil-in-water type, produced with the use of clay, yielded a hard surface film on exposure to air, but readily

re-emulsified in the presence of water. On adding titanium salts to the original mixture, however, the film or crust became quite resistant to water.[50]   Suspensions of titanium dioxide in pentane and other media have been applied to subjects to be investigated by Roentgen rays to form a contrast layer.[51]

Molds for metal castings have been faced with a composition consisting primarily of finely divided titanium dioxide bonded with cement to prevent penetration of the molten metal.[52] Powdered titanium nitride applied to the surface of foundry molds and cores gave the surface a high resistance to molten metals and eliminated the necessity for the tedious and expensive cleaning of small parts.[53] Such a composition has a major portion of a siliceous filler such as ground silica and gypsum with 0.1 to 15.0 per cent titanium dioxide incorporated with it to render the mixture more free-flowing.[54] Compositions of titanium were found to be suitable for making molds for dental and jewelry castings. Another refractory mixture for the same purpose contained from 70 to 95 per cent finely divided silica and from 5 to 30 per cent titanium magnesium silicate.[55]

Carbon may be cemented to carbon or to a metal by the formation in place of titanium carbide.[56] The surfaces to be joined were coated with a carbonaceous material such as sugar, starch, or cellulose, and powdered titanium metal, and heated in position in a nonoxidizing atmosphere. A composition consisting of 10 per cent titanium dioxide, 80 per cent magnesium oxide, and 10 per cent barium sulfate, in an aqueous solution of magnesium chloride, has been employed for uniting granular material such as sand and sawdust.[57]

Addition of not over 5 per cent titanium dioxide to Portland cement somewhat improved its physiochemical properties,[58] but higher proportions proved detrimental.

Seamless tubes of titanium may be formed by depositing the metal by electrochemical means or by thermal decomposition on a core, and then dissolving the core chemically.[59] Coatings have been produced by depositing the metal, vaporized in an electric arc in a chamber supplied with inert gas under pressure.[60] The vaporized titanium was removed through a hollow electrode.

A protective coat of surface oxidation on magnesium may be produced chemically by the action of solutions of titanates,[61] and an opaque enamel-like coating can be formed on articles of aluminum or its alloys by electrolytic oxidation in a bath containing titanic salts.[62] Better results were obtained from complex salts, or alkali metal, or ammonium double salts, at a pH of 1 to 3.5.

Titanium is used as an inhibitor for ferrous metal tubes of mercury boilers.[63] It forms a very thin coating on the tube surface that is in contact with the mercury.

The solid complex, formed by the combination of methyl ether and anhydrous titanium tetrachloride above 150° C., may be used in electroplating baths or as a condensing agent for accelerating chemical reactions.[64] Newall [65] reported that the tetrachloride inhibits the propagation of the zone of combustion in powdered coal. Titanium metal gives a brilliant white light on burning, and because of this property is used in pyrotechnics.

Bell [66] employed sulfides, selenides, and tellurides of titanium as bearing-surface lubricants. The tetrachloride has been used with phosphoric acid in applying a rust-resisting coating on steel before painting.[67] Pye [68] used a small proportion of titanium sulfate or chloride as a component of a mixture employed for the selective flotation of crystalline sodium sulfate from sodium chloride.

The reaction product of titanium compound with logwood produced a permanent deep black ink which underwent no change after use.

DeHaas and Wiersma [69] reported that cesium titanium alum, $Ce_2SO_4 \cdot Ti_2(SO_4)_3 \cdot 24H_2O$, could be employed in determining the thermodynamic scale of temperature for a large interval below 1° K by magnetic measurements only. From the relative f-values of titanium lines, the temperature of the sun's reversing layer has been calculated to be 4400° K.[70]

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INDEX